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Are Concentration-Discharge Relations Influenced by Water Sample Collection Methods?

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Abstract

Two primary methods of stream water sampling, the U.S. Geologic Survey (USGS) equal-width increment (EWI) and point samples (PS) from vertical centroid of flow (VCF) were compared at three river sites, the White River near Fayetteville, Richland Creek at Goshen, and War Eagle Creek near Hindsville. A little over three years of concentration data, which was paired with corresponding instantaneous discharge values (http://ar.water.usgs.gov/), was gathered separately at each site by the Arkansas Water Resource Center (AWRC) and the United States Geological Survey (USGS). The purpose of this study was to evaluate how concentration is related to discharge when water samples are collected by the two different sampling methods. The measured constituents included nitrate-nitrogen (NO_3-N), dissolved orthophosphorus (soluble reactive phosphorus, SRP), total phosphorus (TP), total nitrogen (TN), and suspended sediment (TSS). A three step process was used to analyze the concentration-discharge relationships: (1) simple linear regression comparison, (2) LOESS residual t-test, and (3) split base and storm flow linear regression comparisons. In addition, an estimation of mean constituent loads and corresponding 95th confidence intervals were calculated using LOAD ESTimator (LOADEST, USGS). In general, PS samples provided results similar to the more rigorous and expensive EWI method. TSS and TN concentrations were significantly lower during storm flow at the White River and War Eagle Creek; however, SRP concentrations gathered by PS sampling method were greater during storm flow at the same two rivers. TP was significantly greater for the PS method during base flow at multiple sites, and combined with SRP results, was most likely due to seasonal variation not captured by the EWI method. Interestingly, no significant differences between methods were shown at Richland Creek for split flow regression comparison. NO_3-N was not significantly different between sampling methods at any of the three sites. While both methods provide similar results under certain conditions,

research goals and sampling method limitations must be full understood in order to obtain accurate measurements.

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Introduction

Watershed management is essential to sustaining valuable water resources; in particular, Beaver Lake watershed services a growing population in Northwest Arkansas, and development along primary tributaries that run in to Beaver Lake are constantly changing point and non-point source inputs (Haggard et al. 2003). Catchment land use has been shown to affect nutrient concentrations and loads in streams during seasonal base flow and storm flows across the United States (Beaulac and Reckhow, 1982; McFarland and Hauck, 1999; Haggard et al., 2003). An accurate measurement of nutrient and sediment concentrations entering in from the watershed via streams to Beaver Lake allows for the representative nutrient transport and loads to be measured.

Water quality in streams is commonly analyzed by the chemical analysis of water samples collected to represent a body of water; however, a more precise view of total stream constituent concentrations can only be determined if a representative measurement is taken from the stream. Increasing the accuracy of constituent concentrations in water samples typically comes at a cost and the pressure between these two sides play an increasingly important role for researchers and watershed managers who need reliable information that stays within the budgets of their funding. There are two commonly used methods for stream sampling each with its own advantages and disadvantages (Hallock 2005).

The United States Geological Survey (USGS) developed the equal width increment (EWI) sampling method in the 1970's as an accurate technique for estimating constituents that may not be homogenous throughout the water column (USGS 2006). Though, due to many stipulations in the methods, funding, and inaccessible bridge access, many research labs opt out of the EWI for the less demanding grab sample (point sample, PS) method of sampling water (Hallock 2005). Some have objected that the extra cost of using the EWI method cannot be justified by the little difference in improved accuracy for particular constituents. Comparison studies between the two methods have been completed in several different locations with varying trends of stream concentration representation.

Numerous papers have reported similar findings on differences between EWI and PS sampling methods. Constituents such as total phosphorus (TP) and suspended solids (total suspended solids, TSS from here on out) that are not homogenously distributed throughout the water column were under-represented in the PS sampling method (Martin, 1992; Lietz, 1999; Ging, 2003); TSS and TP are vertically and horizontally distributed because TSS consists of different sized and density materials while fluvial velocities vary in the cross section (Horowitz, 2013). However, these same sites had relatively small sample sizes for each site location within the study (observations ≤ 21). On the other hand, no differences were found in the nitrogen concentration results. In a study by Kammerer (1998), significant differences between methods were shown in suspended sediment; moreover, orthophosphate (SRP from here on out) was significantly different while TP was not. This study showed that variability was not as great of a factor between EWI and PS sampling methods, but rather with-in laboratory variability was significantly different. Kammerer showed that the reliable but costly EWI water sampling method may not be as representative of stream constituent concentrations as previously thought simply due to the lab error. Other factors can influence differences between integrated and grab sample methods.

According to Harmel (2010), integrated samples along the cross-section of the stream better represents within-channel variability, but this procedure does not capture temporal variability unless it is repeated during each high flow (storm) event. Seasonality affects the bioavailability of the dissolved constituents of TN and TP, NO_3-N and SRP, making it more difficult to measure long-term trends in concentrations when the EWI sampling method is used ten times a year at one site. The PS sampling method may not represent the concentration across the entire cross section of the stream, but major seasonal trends can be seen when weekly water samples with storm chasing samples are gathered.

The objective of this study was to evaluate how concentration is related to discharge when water samples are collected by the two different sampling methods (EWI and PS). Five constituents (TN, NO_3, TP, SRP, TSS) were sampled by both methods and analyzed across three streams in the Beaver Lake watershed. A progression of analysis was used to describe differences in the constituent concentrations between the two sampling methods, including (1) comparison of slope and intercept from log-log regressions, (2) comparison of residuals from LOESS, and (3) then comparison of regression during base flow and storm event conditions. Varying investigative techniques into the concentration-discharge relationship allowed for an appropriate interpretation of trends in the constituents. This analysis helped evaluate how each sampling method represents the stream concentrations, seasonal variation, differences between streams, and the potential benefits of either sampling method for short or long-term studies.

Methods

Study Site Description

The Beaver Lake Watershed, situated in the Ozark Mountains, is the water supply for approximately 350,000 people and various industries in northwest Arkansas. There are several water districts pulling raw water from Beaver Lake, including Beaver Water District, Benton-Washington Regional Public Water Authority, Carroll Boone Water District, and Madison County Regional Water District. This watershed and Beaver Lake are regionally important, providing mainly water supply, flood control (via the U.S. Army Corps of Engineers), and recreational opportunities. The reservoir has been the focus of various limnological investigations and hydrodynamic-water-quality models (e.g., Haggard et al., 1999; Haggard and Green, 2002; Galloway and Green, 2007; De Lanois and Green, 2011; Sen et al., 2007). The streams and rivers draining the watershed have also been the focus of investigations on nutrient transport, the influence of municipal effluent discharge, and the effects of land use on stream sediment and water nutrients (e.g., Haggard et al., 2003; Migliaccio et al, 2007; Hufhines et al., 2011; Giovannetti et al., 2013; Chaubey et al., 2005; Leh and Bajwa, 2007).

Three stream sites were selected in the Beaver Lake Watershed including these three sites, the White River near Fayetteville (USGS station 07048600), Richland Creek at Goshen (USGS station 07048800), and War Eagle Creek near Hindsville (USGS station 07049000). These three sites drain the majority of the catchment area (70%) in the Beaver Lake Watershed (~2,080 km^2, Figure 1). The White River has the largest drainage basin (1,040 km^2) followed by War Eagle Creek (681 km^2) and finally Richland Creek (357 km^2). The three streams are monitored and updated on-line every 15 minutes for stream discharge (cfs) to the USGS web site (http://ar.water.usgs.gov/). These streams have been monitored for constituent concentrations for the last decade or longer by two organizations, the USGS Arkansas Water Science Center and the Arkansas Water Resources Center (AWRC) within the University of Arkansas System. Since 2009, these two organizations have been collecting water samples using two different protocols from the bridges crossing these three rivers.

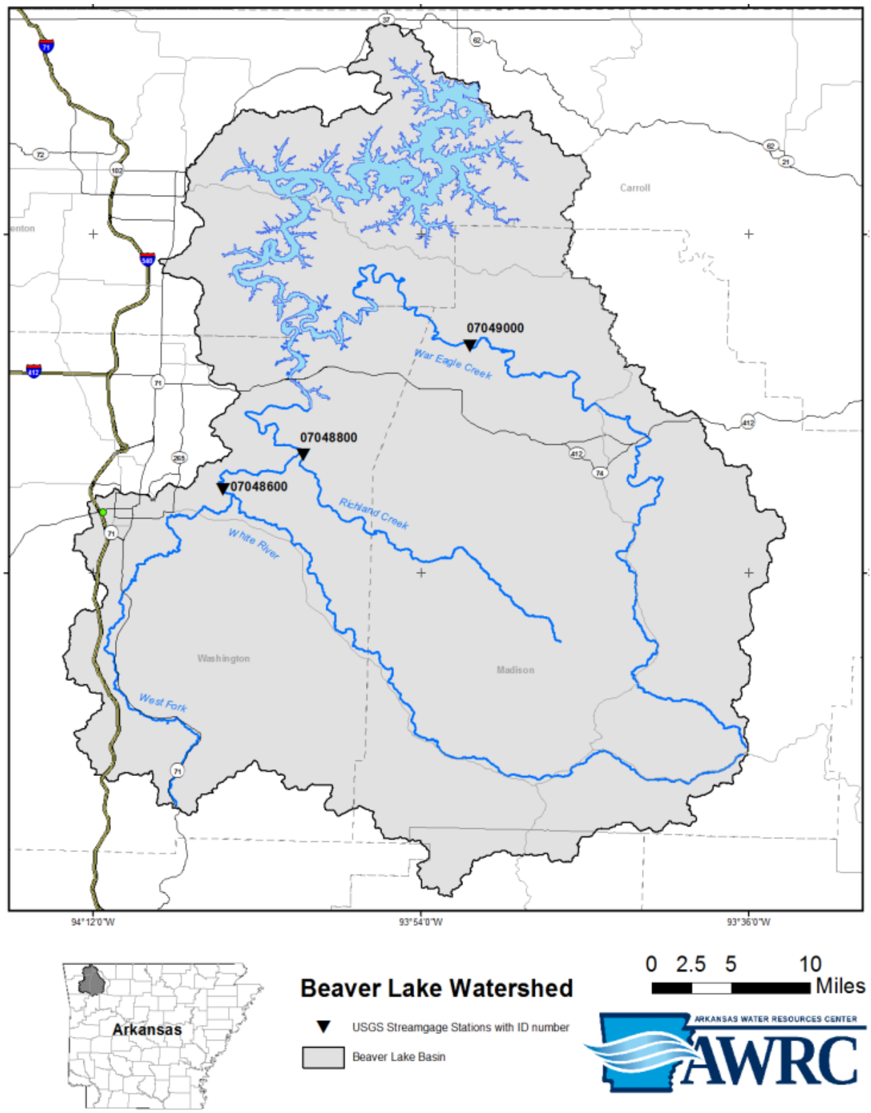

Figure 1- Location of study sites in Beaver Lake Watershed

Water Sample Collection and Analysis

Arkansas Water Resources Center

Since 2009, the AWRC has been collecting grab or point samples from the bridges spanning these rivers at the vertical centroid of flow (VCF). Point sampling or samples (PS) is a common method performed by hand with a bottle submerged in wadeable streams or using an alpha sampler (for example) to collect a water sample from a single point just under the water surface where water is actively moving and likely well-mixed. Water samples have been collected approximately 46 times per year at these three streams during base flow conditions, as well as targeting the peak of the storm event hydrograph during select events. The target has been having approximately 25 percent of collected water samples be during storm events, which varies annually depending upon precipitation frequency and intensity. Water was collected using an alpha sampler from the VCF and then immediately chilled in an ice-chest.

The water samples are transported back to the AWRC Water Quality Lab, which is certified by the Arkansas Department of Environmental Quality. Water samples are split, filtered, preserved and stored following the lab's quality assurance plan, and then analyzed for soluble reactive P (SRP), total P (TP), nitrate-N (NO_3-N), total N, and total suspended solids within appropriate holding times. The analytical procedures follow standard methods for the analysis of water samples, and the details can be found at http://www.uark.edu/depts/awrc/ waterqualitylab.html. In summary, unfiltered water was digested using the autoclave persulfate method (APHA 4500P), and then TP was analyzed using the ascorbic acid method on a spectrophotometer (EPA 365.2, Beckman Coulter Model DU 720) and TN using cadmium copper reduction on a Lachet 8500 or Skalar San Plus auto-analyzer (APHA 4500 PJ). NO_3-N was analyzed using ion chromatography on unfiltered raw samples (EPA 300.0, Dionex ICS

1600). The ascorbic acid method (EPA 365.2) was used to determine the SRP on acidified, filtered (0.45 µm) water samples. TSS was analyzed on raw water samples using a 1.5 micron glass fiber filters (934-AH filter) and weighed to determine the concentration (EPA 160.2).

U.S. Geologic Survey

The USGS collects water samples from these three streams using the EWI sampling method, which requires the cross-section of the stream to be split into an equal number of verticals (usually a minimum of 10 and a maximum of 20 increments). The vertical samples across the cross section are split using a churn to produce a composite water sample, representing the cross section. At low base flow where the sampler cannot be fully submerged, a representative sample may be taken with a handheld bottle at the VCF. During high-flow events, a reduced number of verticals are necessary due to rapidly changing stage and the ability to collect a larger number of samples from multiple locations (USGS, 2006).

The USGS Arkansas Water Science Center mails the composite samples to the USGS National Water Quality Laboratory (http://nwql.usgs.gov/). The water quality data was retrieved from the USGS National Water Information System (NWIS), and the parameters of interest included Ortho-P (USGS parameter code 00671), TP (parameter code 00665), NO_3-N (parameter code 00618), TN (parameter code 00600), and SSC (parameter code 80154). These parameters codes were selected because these most closely match the data collected by the AWRC, although there are some slight differences in analytical techniques. For example, the AWRC measures SRP whereas the USGS NWQL measures ortho-phosphate (PO_4-P), and PO_4-P is a component of SRP. Furthermore, the USGS NWQL also measures SSC whereas the AWRC measures TSS. Despite, the slight analytical differences these data were compared directly against each other in the following data analysis.

Data Analysis

Concentration data (TN, NO_3-N, SRP, TP, and TSS) from the AWRC and USGS were paired with corresponding 15-minute increment discharge values gathered from USGS discharge monitoring stations. Due to the large range in magnitudes, all of the data including concentrations and discharge were natural log-transformed; log transformations are commonly used when viewing and analyzing water quality data (Hirsch, Alexander, and Smith, 1991). The log-transformed concentration (mg/L) and discharge (cfs) were the basis of the various statistical comparisons used to compare sampling methods (Figure 2A).

The first step was to compare concentration collected by the two sampling methods (PS and EWI) with discharge using linear regression (least squares) and log-transformed data (Figure 2B). The slopes and intercepts of the two regression lines were compared (Statistix 9.0, Tallahassee, FL) to evaluate whether the sampling method had a significant influence on the relation between concentration and discharge. Analysis of covariance was used to evaluate if the concentrations from either method were equal across similar discharge ranges. An alpha (α) of 0.05 was used for these statistic comparisons and all subsequent tests. However, this assumes that the change in concentration with discharge is linear and several studies have shown that this relation is non-linear (Lettenmaier, 1976; Hirsch et al., 1982; Helsel and Hirsch, 2002).

Since concentration-discharge relations are often not linear, locally weighted scatterplot smoothing (LOESS) was used to estimate this curve (Systat Software, Inc., San Jose, CA) (Figure 2C). This process requires that a smoothing factor (f) be defined, which was set at 0.5 ($f = 0.5$) in Sigmaplot. Bekele and McFarland (2004) suggested that the default value ($f = 0.5$) was adequate for reducing variability in constituent concentrations due to flow; this was also verified by incrementally increasing f in this study (data not shown). Sigmaplot also allows for the polynomial degree and rejection of outliers, where this study used a degree of one and did not reject outliers. The residuals from the LOESS line are often used as flow adjusted concentrations in trend analysis (White et al., 2004; Scott et al., 2011). Assuming equal variance, the residuals were compared in this study using a t-test to determine if there was a difference between sampling methods (EWI and PS). The t-test assumed normal distributions, which was often not met based on the Shapiro-Wilk statistic ($p<0.05$). When the normal distribution was not met, a non-parametric procedure (Wilcoxin-Mann Whitney rank sum test) was used to determine if the residuals from the two sampling methods were different. In addition, the line produced by the LOESS smoothing suggested a change in the curve where base flow shifted to storm event conditions.

Stream water quality can be influenced differently at base and storm flow conditions by natural or anthropogenic point and nonpoint source pollutions (White et al., 2004). Therefore, separate linear regression (least squares) analysis was used to compare concentrations at different flow regimes. The breakpoint between the two flow conditions was determined from the LOESS curve, where an obvious shift in the concentration-discharge trend occurred (Figure 2D). The slopes and intercepts of the two regression lines for both base flow and storm event conditions were compared (Statistix 9.0) to determine differences between sampling methods.

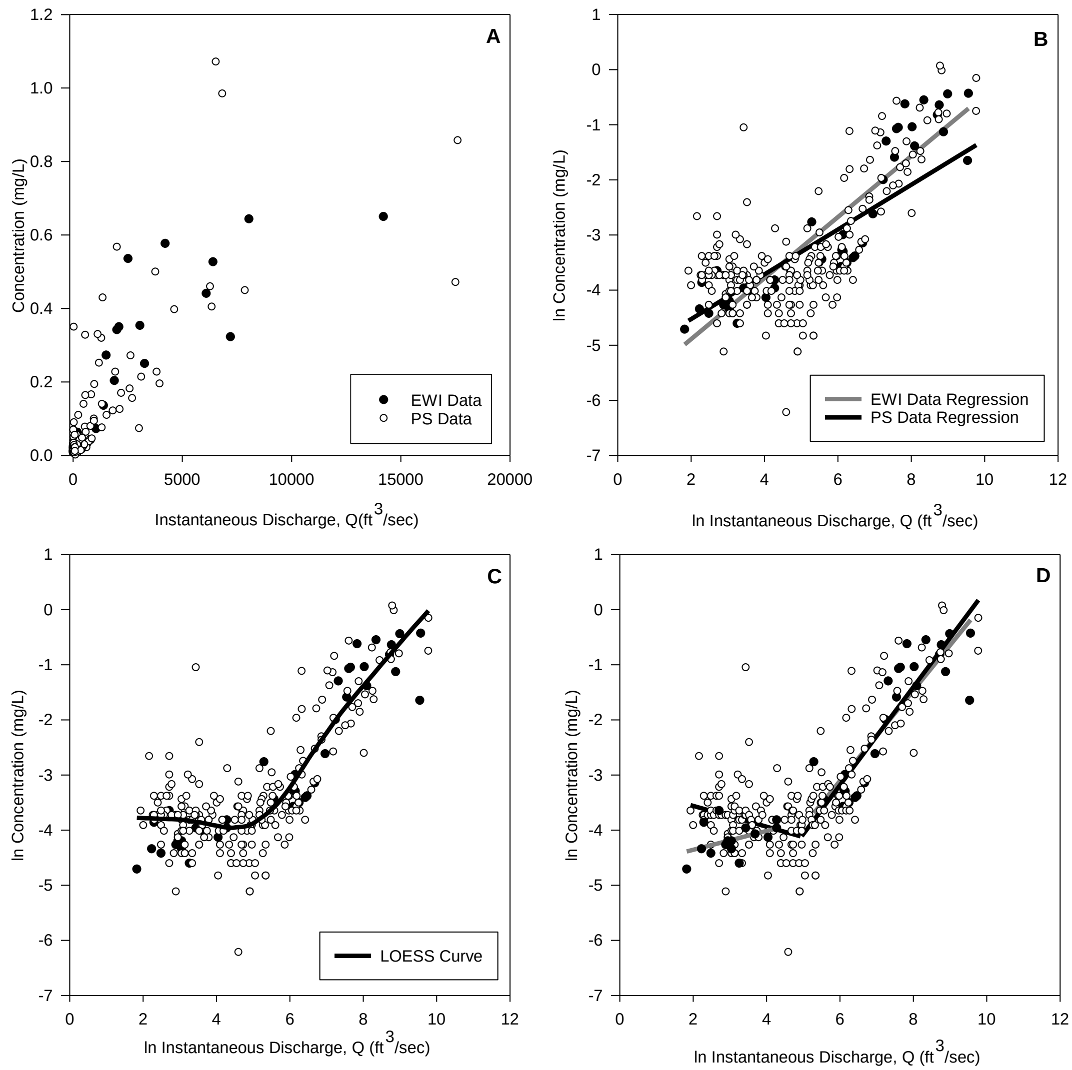

Figure 2- Steps of data analysis performed on concentration-discharge data.

For the stream discharge and constituent concentrations, an estimation of constituent loads was developed using LOAD ESTimator (LOADEST, USGS). Mean load estimates and 95 percent confidence intervals (kg/d) were developed using the adjusted maximum likelihood estimation (AMLE), which is appropriate when the data set contains censored data. Regression models 1 and 4 were performed in LOADEST for each data set in order to determine constituent loads as a result of a linear relationship (model 1) or seasonal factors (model 4) in the discharge-concentration relationship.

Results

Richland Creek

Sample Count and Discharge

A total of 30 EWI samples were collected by the USGS, whereas 136 water samples were collected by the AWRC during the study period. Discharge was not available from October 2009 to June 2010 from the USGS online database, resulting in the least number of paired observations (concentration and discharge) at Richland Creek relative to the other two study sites. The instantaneous discharge (Q_i, ft^3/s) ranged from <1 to 3,930 ft^3/s associated with water samples collected by the AWRC, and the range (<1 – 3,920 ft^3/s) was similar for the EWI samples. Interestingly, the highest flow sampled by both agencies was taken 15 minutes apart on March 20, 2012. The AWRC collected 60% of the water samples during base flow conditions, whereas only 40% of the EWI samples were collected base flow, showing that storm events were adequately samples by both agencies.

Nitrogen (Total and Nitrate)

The mean and standard deviation for TN and NO_3-N concentrations (mg/L) were comparable between sampling methods. For TN, the mean concentration in EWI and PS water samples were 1.442 and 1.107 mg/L, and standard deviations were 0.882 and 0.763, respectively. Mean NO_3-N concentration in EWI and PS water samples was 0.849 and 0.891 mg/L, and standard deviations were 0.658 and 0.733, respectively. Nitrogen concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 1).

For the two sampling methods, discharge (Q_i) explained greater than 40% of the variability in nitrogen concentrations (log-transformed, linear regression, $P<0.01$). The slope and intercepts of the linear regressions for TN, NO_3-N and Q_i were not significantly different ($P>0.05$) between the data collected by each sampling method (Table 1). However, a clear pattern in the residuals existed suggesting that the increase in concentration with increasing discharge was not necessarily monotonic.

Locally weighted scatterplot smoothing (LOESS) was used to define the non-linear relation between log-transformed nitrogen concentrations and discharge, showing that concentrations increased at low flow and then tended to level off at higher flows. The mean of the residuals from LOESS were not significantly different between the sampling methods for TN (t-test, $P=0.20$) or NO_3-N ($P=0.74$); however, the residuals failed the Shapiro-Wilk normality test (SWNT, $P<0.05$). The residuals were also compared non-parametrically, showing that the means were not significantly different for TN ($P=0.10$) or NO_3-N ($P=0.58$). The LOESS smoothing line followed an s-curve relationship with the greatest increase in concentration occurring between <1 and 37 (ft^3/s) before plateauing at high discharges. LOESS regression curve of NO_3-N concentrations was similar in manner to the curve of TN, yet the regression curve began to decrease linearly at high discharge.

The mid-point of the LOESS curve (37 ft^3/s) was chosen as the breakpoint to separate the nitrogen concentrations into that from seasonal base flow conditions and high flow events (i.e., storm flow). Linear regressions between log-transformed nitrogen concentrations and discharge were significant ($P\leq0.01$) during base flow conditions, where discharge explained 33% or more of the variability in nitrogen concentrations (Table 1). The slopes and intercepts of the linear regressions using nitrogen concentrations during base flow conditions were not significantly different ($P \geq 0.26$). The linear regressions of log-transformed data during high flow conditions were significant for NO_3-N ($P \leq 0.01$) across the sampling methods (Table 1), but not for TN ($P \geq 0.52$). The slopes and elevations for the linear regressions during high flow were not significantly different for either sampling method ($P \geq 0.07$).

Phosphorus (Total and SRP)

The mean and standard deviation for phosphorus concentrations (mg/L) were numerically different between constituents (SRP and TP) and sampling methods (EWI and PS). For TP, the mean concentration in EWI and PS water samples were 0.139 and 0.319 mg/L, and standard deviations were 0.181 and 1.045, respectively. Mean SRP concentration in EWI and PS water samples was 0.027 and 0.014 mg/L, and standard deviations were 0.050 and 0.027, respectively. The mean concentrations (and standard deviation) were numerically greater for TP for the PS sampling method, but less for SRP. However, phosphorus concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 2).

For the two sampling methods, discharge (Qi) explained greater than 31% of the variability in phosphorus concentrations (log-transformed, linear regression, $P<0.01$). The slope and intercepts of the linear regressions for TP, SRP and Qi were not significantly different ($P>0.06$) between the data collected by each sampling method (Table 2). A distinct pattern in the residuals existed showing that the increase in concentration with increasing discharge was not necessarily a straight line, especially for the concentrations from the PS sampling method which had over four times the number of samples.

LOESS was used to define the non-linear relation between log-transformed phosphorus concentrations and discharge, displaying that concentrations stayed level at low flow and then increased at higher flows. The mean of the residuals from LOESS were not significantly different between the sampling methods for SRP (t-test, P=0.53), whereas the residuals for TP were significantly different (P=0.04). However, the residuals failed the test for normality (SWNT, P<0.05), and the non-parametric comparison also showed that the residuals were not significantly different between sampling methods for SRP (P=0.83) but were significantly different for TP (P=0.03). The residuals for TP concentrations were greater for the PS sampling method (0.07) relative to the concentrations measured via the EWI sampling method (-0.44). The LOESS smoothing line showed that concentrations tended to decrease slightly during low flow conditions, and then the greatest increase in concentrations occurred after 37 and 20 ft^3/s for SRP and TP, respectively. The LOESS curve of SRP concentrations was similar to the curve of TP, yet neither curve was linear at low flows.

The mid-point of the LOESS curve for SRP and TP (37 and 20 ft^3/s, respectively) was chosen as the breakpoint to separate the phosphorus concentrations into that from base flow conditions and high flow events. During base flow conditions, linear regressions between log-transformed TP concentrations and discharge were significant (P≤0.01) for PS water samples but not EWI water samples (P=0.42). In contrast, SRP concentrations did not increase linearly with base flow discharge for either sampling method (log-transformed data, linear regression, P>0.92). However, discharge only explained 5% of the variability in TP concentrations during base flow conditions (Table 2). The slopes and intercepts of the linear regressions between phosphorus concentrations and base flow discharge were not significantly different (P≥0.14). The linear regressions of log-transformed data during high flow conditions were significant for phosphorus concentrations ($P<0.01$) across the sampling methods (Table 2). The slopes and elevations for the linear regressions during high flow were not significantly different between the sampling methods ($P \geq 0.14$).

Total Suspended Solids

The mean and standard deviation for TSS concentrations (mg/L) were numerically greater for the EWI sampling method when compared to the PS method. The mean concentration in EWI and PS water samples were 141 and 34 mg/L, and standard deviations were 215 and 89, respectively. Similar to other constituents, TSS concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 3).

For the two sampling methods, discharge (Q_i) explained greater than 40% of the variability in suspended solids concentrations (log-transformed, linear regression, $P<0.01$). The slope of the linear regression for TSS and Q_i was not significantly different ($P=0.18$) between the data collected by each sampling method, however the elevation of the linear regression was significant ($P<0.01$) (Table 3); the elevation of the linear regression for TSS and Q_i was greater for the EWI sampling method (0.24) relative to the elevation of the PS sampling method (-0.23). Although the two sampling methods (EWI and PS) showed differences in the elevation of the linear regression, a distinct pattern in the residuals existed displaying that the increase in concentration with increasing discharge was not necessarily linear, especially for the data rich PS sampling method.

LOESS was used to define the non-linear relation between log-transformed TSS concentrations and discharge, showing that concentrations stayed relatively level at low flow and increased at higher flows. The mean of the residuals from LOESS were significantly different between the sampling methods for TSS (t-test, $P=0.02$), and the residuals passed the test for normality (SWNT, P=0.51). The residuals for TSS concentrations were greater for the EWI sampling method (0.35) relative to the concentrations measured via the PS sampling method (-0.16). The LOESS smoothing line showed that concentrations tended to decrease slightly during low flow conditions, and then the greatest increase in concentrations occurred after 53 ft^3/s.

The mid-point of the LOESS curve (53 ft^3/s) was chosen as the breakpoint to separate the suspended solid concentrations into that from low flow conditions and high flow events. During base flow conditions, linear regression between log-transformed TSS concentrations and discharge was significant (P=0.05) for PS water samples but not EWI water samples (P=0.35); however, discharge only explained 2% of the variability in TSS concentrations during base flow conditions (Table 3). The slopes and intercepts of the linear regressions between TSS concentrations and base flow discharge were not significantly different (P≥0.14). The linear regressions of log-transformed data during high flow conditions were significant for TSS (P<0.01) across the sampling methods, where discharge explained 68% of the variability in suspended solid concentrations during storm flow (Table 3). The slopes and elevations for the linear regressions during high flow were not significantly different between the sampling methods (P≥0.11).

Loads (LOADEST)

The mean annual discharge through the study period (2009-2013) was 169 ft^3/s. Previous studies that conducted load estimations (1999-2008) showed similar average discharge of 176 ft^3/s (Bolyard et al, 2010).

TN mean load estimates ranged from 500 to 550 kg/d for both models and sampling methods (Table 10,11). An earlier USGS study (Bolyard et al, 2010) calculated a mean load of 600 kg/d, which was within the 95th confidence intervals (350-680 kg/d) of both models and sampling methods. Nitrate mean load estimates made up greater than 69% of TN load estimates from the EWI sampling method, while Nitrate load estimates from PS method were slightly greater than TN load estimates. Nitrate mean load estimates ranged between models from 410 to 440 kg/d for the PS method and 600 to 800 kg/d for the EWI method (Table 10,11). The previous value from a USGS study (630 kg/d) fell within the 95th confidence intervals (320-840 kg/d) for all models and sampling methods (Bolyard et al, 2010).

Mean load estimates for TP were 60 kg/d for both models for the EWI sampling method and ranged from 70 to 130 kg/d for the PS method. A previous study by Bolyard et al (2010) calculated a mean load estimate of 25 kg/d, which was less than half the lower mean load estimates of this study; however, the 95th confidence intervals (18-140 kg/d) from both models and sampling methods were within the range (Table 10,11). SRP mean load estimates made up less than 13% of the TP load estimates for both sampling methods and models. Mean load estimates ranged from 7 to 8 kg/d for both sampling methods and models. The USGS value provided by Bolyard et al (2010) (6 kg/d) was within the 95th confidence intervals (4-14 kg/d) for both models and sampling methods (Table 10,11).

Mean load estimates for TSS were between 20,000 and 26,000 kg/d for the PS method, while the EWI method was 70,000 for both models. Both models and sampling methods 95th confidence intervals (8,700-80,000) were within the USGS previous study value 26,767 kg/d (Bolyard et al 2010) (Table 10,11).

Table 1- Results from linear regression and comparison of slope and elevation for nitrogen concentrations between samples collected using equal width increment (EWI) and single points (PS) from Richland Creek.

	Total Nitrogen (TN)			Nitrate (NO_3-N)		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All Data						
Observations	30	134		30	136	
R^2	0.705	0.475		0.424	0.410	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.255	0.259	0.932	0.333	0.393	0.468
Elevation (mg/L)	-1.022	-1.041	0.977	-2.179	-1.998	0.053
Base Flow Data						
Observations	12	79		12	80	
R^2	0.479	0.333		0.670	0.500	
P-value (regression)	0.013	<0.001		0.001	<0.001	
Slope (mg/L)	0.431	0.398	0.860	1.251	0.907	0.258
Elevation (mg/L)	-1.288	-1.308	0.750	-3.405	-2.876	0.845
Storm Flow Data						
Observations	18	55		18	56	
R^2	0.026	0.004		0.439	0.111	
P-value (regression)	0.521	0.655		0.003	0.0112	
Slope (mg/L)	0.048	0.019	0.747	-0.309	-0.128	0.094
Elevation (mg/L)	0.332	0.318	0.074	1.982	0.878	0.797

Table 2 - Results from linear regression and comparison of slope and elevation for phosphorus concentrations between samples collected using equal width increment (EWI) and single points (PS) from Richland Creek.

	Phosphate (SRP)			**Total Phosphorus (TP)**		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All Data						
Observations	30	135		30	132	
R^2	0.623	0.438		0.686	0.319	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.350	0.363	0.849	0.499	0.449	0.639
Elevation (mg/L)	-5.999	-6.399	0.0631	-5.321	-4.892	0.438
Base Flow Data						
Observations	12	79		12	78	
R^2	0.0012	5E-05		0.0081	0.0548	
P-value (regression)	0.915	0.952		0.419	0.006	
Slope (mg/L)	0.00269	0.00459	0.993	0.0480	-0.180	0.350
Elevation (mg/L)	-5.488	-5.787	0.200	-4.624	-3.923	0.139
Storm Flow Data						
Observations	18	56		18	54	
R^2	0.503	0.531		0.694	0.228	
P-value (regression)	0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.722	0.719	0.988	1.070	0.761	0.427
Elevation (mg/L)	-8.438	-8.363	0.820	-9.067	-6.450	0.143

Table 3 - Results from linear regression and comparison of slope and elevation for total suspended solids concentrations between samples collected using equal width increment (EWI) and single points (PS) from Richland Creek.

	Total Suspended Solid (TSS)		
	EWI	PS	P-value (comparison)
All data			
Observations	29	136	
R^2	0.710	0.405	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	0.667	0.524	0.187
Elevation (mg/L)	0.235	-0.231	<0.001
Base Flow Data			
Observations	13	88	
R^2	0.020	.008	
P-value (regression)	0.354	0.045	
Slope (mg/L)	0.104	-0.080	0.477
Elevation (mg/L)	1.083	0.889	0.139
Storm Flow Data			
Observations	16	48	
R^2	0.679	0.739	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	1.446	1.566	0.701
Elevation (mg/L)	-4.955	-6.255	0.110

White River

Sample Count and Discharge

A total of 42 EWI samples were collected by the USGS, whereas 217 water samples were collected by the AWRC during the study period. The instantaneous discharge (Q_i, ft^3/s) ranged from <1 to 35,300 ft^3/s associated with water sample collected by the AWRC, and the range (<1 – 22,800 ft^3/s) was collected for the EWI samples. The AWRC collected 65% of the water samples during base flow conditions, whereas only 40% of the EWI samples were collected during base flow, suggesting that storm events were adequately samples by both agencies.

Nitrogen (Total and Nitrate)

The mean and standard deviation for NO_3-N concentrations (mg/L) were comparable between sampling methods (EWI and PS), but the mean and standard deviation of TN concentrations were numerically greater for the EWI sampling method when compared to the PS method. For TN, the mean concentration in EWI and PS water samples were 0.953 and 0.645 mg/L, and standard deviations were 0.480 and 0.352, respectively. Mean NO_3-N concentration in EWI and PS water samples was 0.413 and 0.394 mg/L, and standard deviations were 0.261 and 0.293, respectively. Nitrogen concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 4).

For the two sampling methods, discharge (Q_i) explained greater than 24% of the variability in nitrogen concentrations (log-transformed, linear regression, $P<0.01$). The slope and intercepts of the linear regressions for NO_3-N and Q_i were not significantly different ($P>0.38$) between the data collected by each sampling method, whereas TN and Q_i were significantly different ($P<0.02$) (Table 4). The slope and intercepts of the linear regressions for TN and Q_i were greater for the EWI sampling method (0.14 and -0.95) relative to the PS method

(0.08 and -0.95, respectively). A clear pattern in the residuals existed suggesting that the increase in concentration with increasing discharge was not necessarily monotonic.

LOESS was used to define the non-linear relation between log-transformed nitrogen concentrations and discharge, showing that TN concentrations increased at low flow and then tended to level off at higher flows; however, NO_3-N concentrations increased over the range of discharge. The mean of the residuals from LOESS were not significantly different between the sampling methods for TN (t-test, $P=0.09$) or NO_3-N ($P=0.94$). Yet, the residuals failed the test for normality (SWNT, $P<0.05$), and the non-parametric comparison also showed that the residuals were not significantly different between sampling methods for NO_3-N ($P=0.99$) but were significantly different for TN ($P\leq0.01$). The residuals for TN concentrations were greater for the EWI sampling method (0.23) relative to the concentrations measured via the PS sampling method (-0.08). The LOESS smoothing line described different non-linear relationships between TN and NO_3-N with the greatest increase in concentration for NO_3-N occurring before 500 ft^3/s, while TN concentration increased the greatest after 500 ft^3/s.

The mid-point of the LOESS curve (500 ft^3/s) was chosen as the breakpoint to separate the nitrogen concentrations into that from base flow conditions and high flow events. During base flow conditions, linear regressions between log-transformed nitrogen concentrations and discharge were significant ($P\leq0.02$), where discharge explained 33% of the variability in nitrogen concentrations from the EWI sampling method; however, discharge explained only 6% of the variability from the PS sampling method, but the PS sampling method had over eight times the number of samples (Table 4). The slopes and intercepts of the linear regressions between nitrogen concentrations and base flow discharge were not significantly different ($P\geq0.16$). The linear regressions of log-transformed data during high flow conditions were significant for TN concentrations ($P<0.01$) across the sampling methods but not for NO_3-N concentrations ($P\geq0.06$) (Table 4). The slopes and elevations for the linear regressions during high flow were not significantly different in between the sampling methods for NO_3-N ($P\geq0.39$), but elevation was significantly different for TN ($P<0.01$). The intercept of the linear regression during high flow for TN was greater for the PS sampling method (-1.25) relative to the EWI method (-1.35).

Phosphorus (Total and SRP)

The mean and standard deviation for phosphorus concentrations (mg/L) were numerically different between constituents (SRP and TP) and sampling methods (EWI and PS). For TP, the mean concentration in EWI and PS water samples were 0.128 and 0.087 mg/L, and standard deviations were 0.153 and 0.152, respectively. Mean SRP concentration in EWI and PS water samples were 0.013 and 0.008 mg/L, and standard deviations were 0.016 and 0.011, respectively. The mean concentrations were numerically greater for phosphorus for the EWI sampling method, whereas standard deviations were relatively similar. Phosphorus concentrations generally increased across the range of sampled flow for both sampling methods (Table 5).

For the two sampling methods, Qi explained greater than 18% of the variability in phosphorus concentrations (log-transformed, linear regression, $P<0.01$). The slope of the linear regressions for SRP and Qi was not significantly different ($P=0.88$) between the data collected by each sampling method, but the elevation was significantly different ($P<0.01$). The elevation of the linear regressions for TP and Qi was not significantly different ($P=0.13$) between sampling methods, but the slope was significantly ($P=0.05$) greater for the EWI sampling method (0.26) due to the much larger sample size taken at base flow by the PS method (0.17) (Table 5). The elevation of the linear regression for SRP was greater for the EWI sampling (-5.61), because the

PS sampling method (-6.13) contained more samples at the lower limits of detection. A distinct pattern in the residuals existed showing that the increase in concentration with increasing discharge was not necessarily linear.

LOESS was used to define the non-linear relation between log-transformed phosphorus concentrations and discharge, showing that concentrations stayed level at low flow and then increased at higher flows. The mean of the residuals from LOESS were not significantly different between the sampling methods for SRP (t-test, P=0.07) or TP (P=0.94). However, the residuals failed the test for normality (SWNT, P<0.05), and the non-parametric comparison also showed that the residuals were not significantly different for SRP (P=0.20) or TP (P=0.22). The LOESS smoothing line showed that concentrations tended to stay level during low flow conditions, and then the greatest increase in phosphorus concentrations occurred after 500 ft^3/s. The LOESS curve of SRP concentrations was similar to the curve of TP, yet neither curve was linear at low flows.

The mid-point of the LOESS curve (500 ft3/s) was chosen as the breakpoint to separate the phosphorus concentrations into that from base flow conditions and high flow events. During base flow conditions, linear regressions between log-transformed phosphorus concentrations and discharge were not significant (P≥0.17), where discharge explained 5% of the variability in phosphorus concentrations (Table 5). The slopes and intercepts of the linear regressions between TP concentrations and base flow conditions were not significantly different (P≥0.10); however, the intercepts of the linear regressions between SRP and base flow were significantly different (P=0.05), while the slopes were not significantly different (P=1.0). The intercept of the linear regression for SRP during low flow was greater for the EWI method (-5.27) relative to the elevation for the PS method (-5.66). The linear regressions of log-transformed data during high flow conditions were significant for phosphorus concentrations ($P \leq 0.02$) across the sampling methods, where discharge explained 23% of the variability in phosphorus (Table 5). The slopes and intercepts for the linear regressions during high flow were not significantly different for the TP sampling method ($P \geq 0.12$) or the elevation for the SRP method ($P=0.56$). However, the slope of the linear regression for SRP during high flow was significantly ($P=0.02$) greater for the PS method (0.70) relative to the slope for the EWI method (0.34).

Total Suspended Solids

The mean and standard deviation for TSS concentrations (mg/L) were numerically greater for the EWI sampling method when compared to the PS method. The mean concentration in EWI and PS water samples were 90 and 38 mg/L, and standard deviations were 118 and 85, respectively. However, TSS concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 6).

For the two sampling methods, discharge (Q_i) explained greater than 46% of the variability in suspended solids concentrations (log-transformed, linear regression, $P<0.01$). The slope of the linear regression for TSS and Q_i was not significantly different ($P=0.10$) between the data collected by each sampling method, however the elevation was significantly different ($P<0.01$) (Table 6); the elevation of the linear regression for TSS and Q_i was greater for the EWI sampling method (1.04) relative to the elevation of the PS sampling method (0.89). A distinct pattern in the residuals existed displaying that the increase in concentration with increasing discharge was not necessarily linear, especially for the PS sampling method.

LOESS was used to define the non-linear relation between log-transformed total suspended solids concentrations and discharge, showing that concentrations stayed relatively level at low flow and increased at higher flows. The mean of the residuals from LOESS were significantly different between the sampling methods for TSS (t-test, $P=0.02$); however, the residuals failed the test for normality (SWNT, $P<0.05$), and the non-parametric comparison also showed that the residuals were significantly different between sampling methods for TSS ($P<0.01$). The residuals for TSS concentrations were greater for the EWI sampling method (0.20) relative to the concentrations measured via the PS sampling method (-0.22). The LOESS smoothing line showed that concentrations stayed relatively constant during low flow conditions, and then the greatest increase in concentrations occurred after 500 ft^3/s.

The mid-point of the LOESS curve (500 ft^3/s) was chosen as the breakpoint to separate TSS concentrations into that from low flow conditions and high flow events. During base flow conditions, linear regression between log-transformed TSS concentrations and discharge was significant ($P=0.05$) for PS water samples but not EWI water samples ($P=0.39$); however, discharge only explained 13% of the variability in TSS concentrations during base flow conditions (Table 6). The slopes and intercepts of the linear regressions between TSS concentrations and base flow discharge were not significantly different ($P\geq0.17$). The linear regressions of log-transformed data during high flow conditions were significant for TSS ($P<0.01$) across the sampling methods, where discharge explained 57% of the variability in suspended solid concentrations during storm flow (Table 6). The slopes and elevations for the linear regressions during high flow were not significantly different between the sampling methods ($P\geq0.10$).

Loads (LOADEST)

The mean annual discharge through the study period (2009-2013) was 556 ft^3/s. Previous studies that conducted load estimations (1999-2008) showed comparable average discharge of 526 ft^3/s (Bolyard et al, 2010).

TN mean load estimates ranged from 1,000 to 1,500 kg/d for both models and sampling methods (Table 10,11). An earlier USGS study (Bolyard et al, 2010) calculated a mean load of 1,600 kg/d, which was within the 95th confidence interval (1,300-1,700 kg/d) of both models for the EWI sampling methods; however, the 95th confidence interval (910-1,100) of both models for the point sample method was outside of the previous USGS study value of 1,600 (Table 10,11). Nitrate mean load estimates made up greater than 48% and 83% of TN load estimates from the EWI and PS sampling methods, respectively. The previous value from a USGS study (750 kg/d) fell within the 95th confidence intervals (710-910 kg/d) for all models and sampling methods (Bolyard et al, 2010).

Mean load estimates for TP ranged from 200 to 210 kg/d for both models for the EWI sampling method, while the PS method ranged from 140 to 160 kg/d for both models (Table 10,11). A previous study by Bolyard et al (2010) calculated a mean load estimate of 200 kg/d. The 95th confidence intervals (140-210 kg/d) were within the range for both models for the EWI sampling method and model four for the point sample method. SRP mean load estimates made up less than 9% of the TP load estimates for both sampling method and models. Mean load estimates ranged from 15 to 19 kg/d for both sampling methods and models. The USGS value provided by Bolyard et al (2010) (28 kg/d) was not within the 95th confidence intervals (14-21 kg/d) for any of the models or sampling methods (Table 10,11).

Mean load estimates for TSS were between 70,000 and 80,000 kg/d for the PS method, while the EWI method was 150,000 for both models. The EWI sampling methods 95th confidence intervals (90,000-260,000) were within the USGS previous study value 190,000 kg/d (Bolyard et al 2010); however, the confidence interval (50,000-100,000) for the point sample method was not (Table 10,11).

Table 4- - Results from linear regression and comparison of slope and elevation for nitrogen concentrations between samples collected using equal width increment (EWI) and single points (PS) from the White River.

	Total Nitrogen (TN)			Nitrate (NO_3-N)		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All Data						
Observations	42	216		42	217	
R^2	0.684	0.249		0.544	0.362	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.136	0.084	0.016	0.202	0.208	0.888
Elevation (mg/L)	-0.950	-0.953	<0.001	-2.311	-2.234	0.388
Base Flow Data						
Observations	17	142		17	142	
R^2	0.333	0.062		0.726	0.326	
P-value (regression)	0.015	0.003		<0.001	<0.001	
Slope (mg/L)	0.115	0.049	0.217	0.424	0.275	0.169
Elevation (mg/L)	-0.898	-0.870	0.227	-2.788	-2.419	0.960
Storm Flow Data						
Observations	25	74		25	75	
R^2	0.410	0.151		0.145	0.020	
P-value (regression)	0.001	0.001		0.060	0.224	
Slope (mg/L)	0.187	0.132	0.425	-0.122	-0.053	0.393
Elevation (mg/L)	-1.353	-1.254	<0.001	0.237	-0.332	0.774

Table 5- - Results from linear regression and comparison of slope and elevation for phosphorus concentrations between samples collected using equal width increment (EWI) and single points (PS) from the White River.

	Phosphate (SRP)			**Total Phosphorus (TP)**		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All data						
Observations	42	217		42	216	
R^2	0.347	0.186		0.577	0.250	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.154	0.161	0.876	0.265	0.174	0.045
Elevation (mg/L)	-5.608	-6.133	.002	-4.180	-3.901	0.126
Base Flow Data						
Observations	17	142		17	142	
R^2	0.008	0.002		0.046	0.013	
P-value (regression)	0.737	0.624		0.409	0.170	
Slope (mg/L)	-0.015	-0.016	0.997	-0.044	-0.29	0.821
Elevation (mg/L)	-5.265	-5.665	0.049	-3.548	-3.361	0.104
Storm Flow Data						
Observations	25	75		25	74	
R^2	0.522	0.231		0.633	0.647	
P-value (regression)	0.015	<0.001		<0.001	<0.001	
Slope (mg/L)	0.344	0.703	0.020	0.627	0.836	0.124
Elevation (mg/L)	-7.084	-10.013	0.557	-7.001	-8.644	0.970

Table 6- Results from linear regression and comparison of slope and elevation for total suspended solid concentrations between samples collected using equal width increment (EWI) and single points (PS) from the White River.

	Total Suspended Solids (TSS)		
	EWI	PS	P-value (comparison)
All Data			
Observations	41	210	
R^2	0.686	0.459	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	0.414	0.324	0.095
Elevation (mg/L)	1.044	0.888	<0.001
Base Flow Data			
Observations	17	138	
R^2	0.051	0.134	
P-value (regression)	0.386	<0.001	
Slope (mg/L)	0.067	0.109	0.591
Elevation (mg/L)	1.769	1.451	0.166
Storm Flow Data			
Observations	24	72	
R^2	0.679	0.571	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	0.889	1.022	0.497
Elevation (mg/L)	-2.701	-4.125	0.103

War Eagle Creek

Sample Count and Discharge

A total of 41 EWI samples were collected by the USGS, whereas 211 water samples were collected by the AWRC during the study period. Discharge was not available from the USGS online database intermittently throughout the study period, resulting in less paired (concentration and discharge) observations at War Eagle Creek relative to the White River, but more paired samples relative to Richland Creek. The instantaneous discharge (Q_i, ft^3/s) ranged from 6.9 to 17,600 ft^3/s associated with water sample collected by the AWRC, and the range (6.2 – 14,200 ft^3/s) was sampled for the EWI samples. Both agencies (AWRC & USGS) collected less than one third of the water samples during base flow conditions, which was the least proportion collected compared to the White River and Richland Creek.

Nitrogen (Total and Nitrate)

The mean and standard deviation for TN and NO_3-N concentrations (mg/L) were comparable between sampling methods. For TN, the mean concentration in EWI and PS water samples were 1.90 and 1.74 mg/L, and standard deviations were 0.70 and 0.58, respectively. Mean NO_3-N concentration in EWI and PS water samples was 1.29 and 1.54 mg/L, and standard deviations were 0.45 and 0.56, respectively. Nitrogen concentrations increased little or not at all with increasing discharge across both sampling methods and the range of flow sampled (Table 7).

For the two sampling methods, Q_i explained 22% of the variability in nitrogen concentrations, but only TN concentrations were significant (log-transformed, linear regression, $P<0.01$) for the EWI method. The slope of the linear regression for NO_3-N and Q_i was not significantly different ($P=0.43$) between the data collected by each sampling method (Table 7), but the intercept was significantly ($P=0.02$) greater for the PS sampling method (0.47) relative to the EWI method (0.44). Conversely, the elevation of the linear regression for TN and Q_i was not significantly different ($P=0.43$) between the data collected by each sampling method (Table 7), but the slope was significantly ($P=0.03$) greater for the EWI sampling method (0.07) relative to the PS method (0.02). Even though simple linear regression provided little evidence of a linear trend, a pattern in the residuals existed suggesting that the increase in concentration with increasing discharge was occurring at low flows, but not necessarily at high flows.

LOESS was used to define the non-linear relation between log-transformed nitrogen concentrations and discharge, showing that concentrations increased at low flow and then tended to level off for TN or even decrease for NO_3-N at higher flows. The mean of the residuals from LOESS was not significantly different between the sampling methods for TN (t-test, $P=0.27$) or NO_3-N ($P=0.29$). The LOESS smoothing lines greatest increase in concentration occurred between <1 and 37 (ft^3/s) before plateauing at higher discharges. LOESS regression curve of NO_3-N concentrations was similar in manner to the curve of TN, yet the NO_3-N regression curve began to decrease linearly at high discharge.

The mid-point of the LOESS curve (37 ft^3/s) was chosen as the breakpoint to separate the nitrogen concentrations into that base flow conditions and high flow events. Linear regressions between log-transformed nitrogen concentrations and discharge were significant ($P\leq0.02$) during base flow conditions, where discharge explained 44% or more of the variability in nitrogen concentrations (Table 7). The slopes and intercepts of the linear regressions using nitrogen concentrations during base flow conditions were not significantly different ($P\geq0.61$). The linear regressions of log-transformed data during high flow conditions were significant for NO_3-N concentrations ($P\leq0.01$) across the sampling methods (Table 7); however, TN was not significant

(P=0.69) for the PS sampling method but was significant (P<0.01) for the EWI method. The slopes and elevations for the linear regressions during high flow were not significantly different for NO_3-N concentrations (P≥0.18), but the slope for TN was significantly different (P=0.02) while elevation was not significantly different (P=0.17). The slope of the linear regressions for TN and Q_i during high flow was greater for the EWI sampling method (0.09) relative to the PS method (-0.01) (Table 7).

Phosphorus (Total and SRP)

The mean and standard deviation for phosphorus concentrations (mg/L) were numerically greater for the EWI sampling method when compared to the PS method. For TP, the mean concentration in EWI and PS water samples were 0.159 and 0.075 mg/L, and standard deviations were 0.202 and 0.148, respectively. Mean SRP concentration in EWI and PS water samples was 0.024 and 0.014 mg/L, and standard deviations were 0.029 and 0.019, respectively. Phosphorus concentrations generally increased with increasing discharge across both sampling methods (Table 8).

For the two sampling methods, Qi explained greater than 45% of the variability in phosphorus concentrations (log-transformed, linear regression, P<0.01). The slope and intercepts of the linear regressions for SRP and Qi were not significantly different (P≥0.06) between the data collected by each sampling method; however, the slope of the linear regression for TP and Qi was significantly different (P≤0.01) while the elevation was not significantly different (P=0.22) (Table 8). The slope of the linear regressions for TP and Qi was greater for the EWI sampling method (0.55) relative to the PS method (0.41). The relation between TP concentration and Qi was not necessarily linear across the range of sampled flow based on the residuals, but SRP showed a monotonic increase over Qi.

LOESS was used to define the non-linear relation between log-transformed phosphorus concentrations and discharge, showing that concentrations stayed level at low flow and then increased at higher flows for TP; however, SRP concentrations stayed linear through the whole range of discharge. The mean of the residuals from LOESS were not significantly different between the sampling methods for SRP (t-test, P=0.18) or TP (P=0.20), yet the residuals failed the test for normality (SWNT, P<0.05) for TP. The non-parametric test for TP was also not significantly different (P=0.17). Decreasing slightly during low flow, the LOESS smoothing lines greatest increase in concentration occurred after 138 ft^3/s for TP, while SRP remained almost linear except for a short downward trend near 138 ft^3/s as well.

The inflection of the LOESS curve for SRP and TP (138 ft^3/s) was chosen as the breakpoint to separate the phosphorus concentrations into that from base flow conditions and high flow events. During base flow conditions, linear regressions between log-transformed SRP concentrations and discharge were significant (P≤0.02) across the sampling methods. TP concentrations increased linearly with discharge for the PS sampling method (P≤0.01); however, concentrations did not increase linearly with discharge for the EWI sampling method (log-transformed data, linear regression, P≥0.11). Discharge explained 8% or more of the variability in SRP concentrations (Table 8). The slopes of the linear regressions were not significantly different (P≥0.09) across the sampling methods at base flow discharge. However, the intercepts of the linear regression were significantly different (P≤0.04) across the sampling methods at base flow discharge. The linear regressions of log-transformed data during high flow conditions were significant for phosphorus concentrations (P<0.01) across the sampling methods (Table 8), where discharge explained 40% or more of the variability. The slopes and elevations for the linear regressions during high flow were not significantly different between the sampling methods ($P \geq 0.11$) (Table 8).

Total Suspended Solids

The mean and standard deviation for TSS concentrations (mg/L) were numerically greater for the EWI sampling method when compared to the PS method. The mean concentrations in EWI and PS water samples were 157 and 32 mg/L, and standard deviations were 248 and 84mg/L, respectively. Still, TSS concentrations generally increased with increasing discharge across both sampling methods and the range of flow sampled (Table 9).

For the two sampling methods, discharge (Q_i) explained greater than 59% of the variability in suspended solids concentrations (log-transformed, linear regression, $P<0.01$). The slope of the linear regressions for TSS and Q_i were not significantly different ($P=0.08$) between the data collected by each sampling method; however, the elevation was significantly (-1.04) greater for the EWI sampling method ($P<0.01$) (Table 9). The elevation of the linear regressions for TSS and Q_i was greater for the EWI sampling method (-1.04) relative to the EWI method (-1.17).

LOESS was used to define the non-linear relation between log-transformed total suspended solids concentrations and discharge, showing that concentrations stayed relatively level at low flow and increased at higher flows. The mean of the residuals from LOESS was significantly different between the sampling methods for TSS (t-test, $P<0.01$); however, the residuals failed the test for normality (SWNT, $P<0.05$). The residuals were also compared non-parametrically, but the means were still significantly different for TSS ($P<0.01$). The residuals for TSS concentrations were greater for the EWI sampling method (0.33) relative to the concentrations measured via the PS sampling method (0.02). The LOESS smoothing line showed that concentrations tended to decrease slightly during low flow conditions, and then the greatest increase in concentrations occurred after 138 ft^3/s.

The mid-point of the LOESS curve (138 ft^3/s) was chosen as the breakpoint to separate the TSS concentrations into that from low flow conditions and high flow events. During base flow conditions, linear regression between log-transformed TSS concentrations and discharge was significant ($P=0.03$) for EWI water samples, but not PS water samples ($P=0.81$) (Table 9). The slopes and intercepts of the linear regressions using TSS concentrations during base flow conditions were not significantly different ($P \geq 0.10$). The linear regressions of log-transformed data during high flow conditions were significant for TSS ($P<0.01$) across the sampling methods, where discharge explained greater than 81% of the variability in suspended solid concentrations during storm flow (Table 9). The slopes for the linear regressions during high flow were not significantly different for either sampling method ($P \geq 0.46$), but the elevation was significantly ($P<0.01$) greater for the EWI sampling method (-4.014) relative to the PS method (-5.364) (Table 9).

Loads (LOADEST)

The mean annual discharge through the study period (2009-2013) was 348 ft^3/s. Previous studies that conducted load estimations (1999-2008) showed a lower average discharge of 294 ft^3/s (Bolyard et al, 2010).

TN mean load estimates ranged from 1,400 to 1,600 kg/d for both models and sampling methods. An earlier USGS study (Bolyard et al, 2010) calculated a mean load of 1,300 kg/d, which was within the 95^{th} confidence interval (1,300-1,600 kg/d) of both models for the PS methods; however, the 95^{th} confidence interval (1,400-1,800) of both models for the EWI sampling method was outside of the previous USGS study value (Table 10,11). Nitrate mean load estimates made up greater than 60% and 84% of TN load estimates from the EWI and PS sampling methods, respectively. The previous value from a USGS study (840 kg/d) was within the 95th confidence interval (840-1,100 kg/d) for model one for the EWI sampling methods; however, confidence intervals for model four for the EWI sampling method and both models for the PS method were not (Bolyard et al, 2010) (Table 10,11).

Mean load estimates for TP were 170 kg/d for both models for the EWI sampling method, while the PS method ranged from 110 to 130 kg/d for both models. A previous study by Bolyard et al (2010) calculated a mean load estimate of 80 kg/d. The 95th confidence interval (75-160 kg/d) for model one of the PS method was within the range of the previous USGS value, but confidence intervals for both models for the EWI sampling method and model four for the PS method were not (Table 10,11). SRP mean load estimates made up less than 23% of the TP load estimates for both sampling method and models. Mean load estimates ranged from 22 to 27 kg/d for both sampling methods and models. The USGS value provided by Bolyard et al (2010) (30 kg/d) was within the 95th confidence intervals (18-31 kg/d) for all models and sampling methods except for model four for the EWI sampling method (Table 10,11).

Mean load estimates for TSS were between 50,000 and 70,000 kg/d for the PS method, while the EWI method was 180,000 for both models. Both models and sampling methods 95th confidence intervals (80,000-90,000) were within the USGS previous study value 80,000 kg/d (Bolyard et al 2010) (Table 10,11).

Table 7- Results from linear regression and comparison of slope and intercept for nitrogen concentrations between samples collected using equal width increment (EWI) and single points (PS) from War Eagle Creek.

	Total Nitrogen (TN)			Nitrate (NO_3-N)		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All Data						
Observations	41	211		41	211	
R^2	0.220	0.008		0.075	0.010	
P-value (regression)	0.002	0.184		0.083	0.151	
Slope (mg/L)	0.0707	0.0162	0.026	-0.044	-0.021	0.427
Elevation (mg/L)	0.167	0.428	0.433	0.444	0.466	0.021
Base Flow Data						
Observations	11	68		11	68	
R^2	0.467	0.439		0.441	0.443	
P-value (regression)	0.020	<0.001		0.026	<0.001	
Slope (mg/L)	0.407	0.458	0.746	0.544	0.570	0.897
Elevation (mg/L)	-0.698	-0.876	0.613	-1.24	-1.34	0.758
Storm Flow Data						
Observations	30	143		30	143	
R^2	0.178	0.001		0.204	0.115	
P-value (regression)	<0.001	0.690		0.012	<0.001	
Slope (mg/L)	0.094	-0.008	0.016	-0.104	-0.092	0.797
Elevation (mg/L)	-0.016	0.569	0.166	0.886	0.907	0.183

Table 8- Results from linear regression and comparison of slope and elevation for phosphorus concentrations between samples collected using equal width increment (EWI) and single points (PS) from War Eagle Creek.

	Phosphate (SRP)			**Total Phosphorus (TP)**		
	EWI	PS	P-value (comparison)	EWI	PS	P-value (comparison)
All Data						
Observations	41	211		41	211	
R^2	0.617	0.451		0.832	0.451	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.309	0.396	0.137	0.554	0.406	0.014
Elevation (mg/L)	-6.016	-6.737	0.069	-5.995	-5.339	0.222
Base Flow Data						
Observations	15	117		15	117	
R^2	0.368	0.078		0.189	0.068	
P-value (regression)	0.016	0.002		0.106	.005	
Slope (mg/L)	0.454	0.295	0.598	0.171	-0.189	0.087
Elevation (mg/L)	-6.383	-6.356	0.036	-4.699	-3.183	0.014
Storm Flow Data						
Observations	26	94		26	94	
R^2	0.402	0.446		0.750	0.756	
P-value (regression)	<0.001	<0.001		<0.001	<0.001	
Slope (mg/L)	0.414	0.512	0.435	0.820	0.890	0.531
Elevation (mg/L)	-6.836	-7.509	0.868	-8.028	-8.528	0.983

Table 9- Results from linear regression and comparison of slope and elevation for total suspended solid concentrations between samples collected using equal width increment (EWI) and single points (PS) from War Eagle Creek.

	Total Suspended Solids (TSS)		
	EWI	PS	P-value (comparison)
All Data			
Observations	38	193	
R^2	0.812	0.591	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	0.762	0.630	0.077
Elevation (mg/L)	-1.036	-1.174	<0.001
Base Flow Data			
Observations	13	104	
R^2	0.379	0.001	
P-value (regression)	0.025	0.811	
Slope (mg/L)	-0.406	-0.017	0.103
Elevation (mg/L)	2.601	1.235	0.304
Storm Flow Data			
Observations	25	89	
R^2	0.805	0.808	
P-value (regression)	<0.001	<0.001	
Slope (mg/L)	1.154	1.256	0.461
Elevation (mg/L)	-4.014	-5.364	<0.001

Table 10 - LOADEST AMLE Load Estimates using model 1. Ex: Mean load (95% confidence interval).

	EWI	PS
	Total Nitrogen (TN)	
Richland Creek	500 (350-710)	550 (350-800)
War Eagle Creek	1,600 (1,400-1,900)	1,400 (1,300-1,600)
White River	1,500 (1,300-1,700)	1,000 (910-1,100)
	Nitrate (NO_3-N)	
Richland Creek	440 (120-1,100)	800 (250-2,000)
War Eagle Creek	970 (840-1,100)	1,200 (1,100-1,300)
White River	740 (550-970)	940 (710-1200)
	Total Phosphorus (TP)	
Richland Creek	60 (15-150)	70 (10-230)
War Eagle Creek	170 (110-250)	110 (75-160)
White River	210 (140-290)	140 (110 -190)
	Phosphate (SRP)	
Richland Creek	8 (4-16)	7 (3-14)
War Eagle Creek	23 (17-31)	25 (17-36)
White River	19 (14-26)	15 (11-21)
	Total Suspended Solids (TSS)	
Richland Creek	70,000 (7,700-290,000)	20,000 (2,000-80,000)
War Eagle Creek	180,000 (80,000-340,000)	50,000 (30,000-90,000)
White River	150,000 (80,000-260,000)	70,000 (40,000-100,000)

Table 11 - LOADEST AMLE Load Estimates using model 4. Ex: Mean load (95% confidence interval).

	EWI	PS
	Total Nitrogen (TN)	
Richland Creek	500 (350-680)	500 (360-690)
War Eagle Creek	1,600 (1,400 – 1,800)	1400 (1,300-1,600)
White River	1,500 (1,300-1,700)	1,000 (900-1,100)
	Nitrate (NO_3-N)	
Richland Creek	410 (170-840)	600 (320-1,000)
War Eagle Creek	990 (850-1,100)	1,200 (1,100-1,300)
White River	720 (560-910)	830 (670-1,000)
	Total Phosphorus (TP)	
Richland Creek	60 (18-140)	130 (15-500)
War Eagle Creek	170 (120-240)	130 (89-200)
White River	200 (140-280)	160 (120-210)
	Phosphate (SRP)	
Richland Creek	8 (4-14)	7 (3-15)
War Eagle Creek	22 (17-29)	27 (18-38)
White River	19 (14-26)	16 (11-23)
	Total Suspended Solids (TSS)	
Richland Creek	70,000(8,700-280,000)	26,000(2,000-110,000)
War Eagle Creek	180,000 (80,000-340,000)	70,000 (40,000-120,000)
White River	150,000 (90,000-260,000)	80,000 (50,000-120,000)

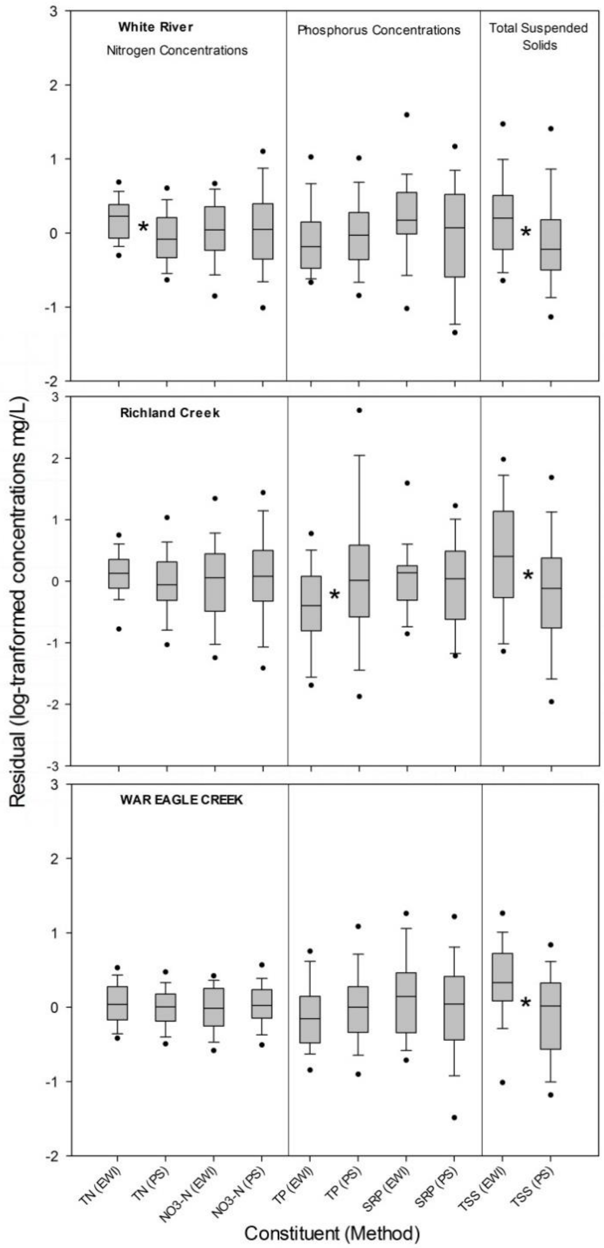

Figure 3 - LOESS residuals (log-transformed concentrations, mg/L) for the EWI and PS sampling methods across all streams and consituents.

Discussion

A three step process was used to identify differences in constituent concentrations between the two sampling methods, including (1) comparison of slope and intercept from log-log regressions, (2) comparison of residuals from LOESS, and (3) then comparison of regression during base flow and storm event conditions. An estimation of constituent loads was made using LOAD ESTimator software. This allowed for load comparisons to other studies and values representing nutrient export over time. The constituent concentrations, in general, were not significantly different with respect to sampling method (EWI and PS) across the range of sampled flow. However, there were some differences that were consistently observed (e.g., sediment concentration) while others (e.g., nutrients) varied by site and were not consistent.

Results from sediment concentrations for all streams sampled were consistent; residuals from the EWI sampling method were greater during storm flow conditions when compared to the PS method. However, separate laboratory techniques were used for processing suspended sediment concentration (SSC, USGS NWQL) and TSS (AWRC). SSC concentrations tend to increase at a greater rate than the TSS concentrations; likewise, SSC exceed paired TSS samples as during high flow events (Kammerer et al., 1998), which is what our split flow regression confirms. Studies comparing the techniques (Gray et al., 2000) have shown TSS concentrations to have a lower bias to SSC by up to 34%. While lab techniques might influence sediment differences, several papers have shown that sediment concentration varies between EWI and PS sampling methods when using the same lab techniques (Martin et al. 1992; Ging 1999). Near surface PS sampling can be lower than EWI sampling due to vertical and horizontal stratification of sediment, and during high flow conditions, differences between methods increases as velocity and carrying capacity of sediment also increases. As expected, sediment loads were greater for the EWI sampling method than the PS method; however, calculated sediment loads from the PS method at Richland Creek and War Eagle Creek were more similar to previous studies by Bolyard et al (2010). The sediment loads from the EWI method at the White River matched previously obtained load data.

Sediment associated constituents such as TP usually show differences between sampling method, because TP is correlated to sediment concentrations. In fact, TSS and TP were positively correlated ($P<0.01$) across all three study rivers. TP residuals were not significantly different between sampling methods at the White River or War Eagle Creek, yet the residuals of the PS method were significantly greater at Richland Creek. Moreover, split flow linear regression comparisons were not significantly different at Richland Creek or the White River, but the elevation of the PS method was greater during low flow at War Eagle Creek. Results suggested that TP concentration were not different between sampling methods at storm flow conditions. This contrasts to the studies by Martin (1992) and Ging (2002) where TP concentrations were significantly different between sampling methods. Differences among methods during low flow at Richland Creek and War Eagle Creek, where TP was greater for the PS method, most likely are due to seasonal variability and large differences in observations rather than bias between sample methods, but seasonal variation typically plays a larger role in the dissolved constituent of TP.

Conversely, SRP concentrations were significantly different between sampling methods during storm flow at the White River and War Eagle Creek. Also, the elevation of the EWI method was greater than the PS method during base flow where differences such as greater method detection limits (MDL) for EWI samples and six times the number of grab samples could account for some of the concentration difference during low flow. Replacing the lower detection limits for the PS sampling method with the detection limits of the EWI sampling method allowed for a more appropriate comparison of sampling methods during base flow conditions. Where significant differences in elevation were observed at the White River between sampling methods at base flow, elevation comparison was not significantly different (P=0.87) once MDL's were changed. In a study by Kammerer et al. (1998), it described similar results that showed significant differences between methods in SRP, but not significant differences in TP. The numerous grab samples showed that there was some seasonality in SRP concentrations, which was not evident in the EWI samples that had much fewer samples taken per year.

While seasonality may have caused differences in sampling method for the dissolved P, for the bioavailable form of nitrogen, NO_3-N, this was not the case. The results for NO_3-N provide evidence that both sampling methods adequately characterize concentrations across all river sites and flows. On the other hand, TN concentrations from the EWI sampling method had a greater slope and elevation for War Eagle Creek and the White River, respectively, during high flow. Moreover, the mean of the LOESS residuals were significantly greater for the EWI method for TN at the White River. In contrast to the results by Lietz (1999) where no difference was found between TN concentrations, it appears that in this study the PS sampling method may under-represent TN concentrations compared to the EWI method during high flow especially at the larger rivers.

Stream size, cross-sectional geometry, and morphological features are important properties when comparing integrated sampling and single point sampling (Hallock, 2005; USGS 2006). Although not measured for this study, the more uniform and shallow cross-section at Richland Creek is more visually obvious than the other two sampled sites, White River and War Eagle Creek, and Richland Creek has a much smaller discharge range over the study period. Having more homogeneity (vertically and horizontally), this may explain the absence of significant differences in the linear regressions for constituents that were significantly different for the other two streams. Moreover, mean load estimations for the same constituents from Bolyard et al (2010) were within the 95th confidence intervals for load estimations at Richland Creek. For Richland Creek, the PS sampling was as representative of the concentrations in the stream cross-section as an integrated EWI sample, but more research would need to be done on similar streams in the Ozarks to confirm these findings.

This study has dealt with how water sampling methods influence the concentration-discharge relationships of constituents, but concentrations alone do not quantify total nutrient and sediment transport that occurs over time. For the purposes of water-quality management in the Beaver Lake Watershed, mean annual constituent loads are estimated from sampled concentrations (Bolyard et al. 2010). This study showed that the mean loads for either sampling method across all constituents were within the 95th confidence interval of the comparable constituent. Ultimately, overestimation can occur when fewer samples are taken during high flow events over longer periods of time rather than more samples throughout different flow conditions (Robertson and Roerish 1999); therefore, a regime of weekly sampling (PS) may be more beneficial for the long-term studies, which better represent seasonal variation in nutrient and sediment loading during storm flow. In a study of the same watershed, Haggard et al (2003) emphasized the need for long term management plans to mitigate excess nitrogen and phosphorus entering the Beaver Lake watershed. For studies that require precision and accuracy of constituent concentrations during a specific time or season, the EWI sampling method might be the preferred technique. For streams in Beaver Lake watershed, ongoing, long-term water quality monitoring may benefit more from frequent, weekly sampling, rather than fixed-period bimonthly sampling. The costs associated with using the more expensive and labor intensive EWI over the point sampling method should be considered by researcher's who cannot exceed their budgets, yet need reliable and cheaper ways of obtaining representative water samples. In general, accurate representation of constituent concentrations varies between sampling methods and at different flow conditions depending on the nature and goals of the research.

Conclusion

We found that little difference was shown between sampling methods at base flow conditions for all streams; the few significant differences that were displayed most likely originated from differences between method detection limits. This provides evidence that EWI sampling does not provide a more accurate representation of constituent concentrations during low flow conditions. Differences between the three streams showed that Richland Creek, which represented the smallest stream in cross-section and discharge range, differed from the other two rivers in that no significant differences between sampling methods at either low or high flow conditions were shown. This indicates that streams with similar characteristics could potentially be sampled by the PS sampling method.

Sediment stratification in larger streams may make the PS sampling method less appropriate for finding TSS where concentrations were underrepresented during high flow conditions; however, differences in lab analysis was important to observe for this study. Contrary to similar research, sediment associated constituent TP was not significantly different during high flow; however, TP concentrations were greater for the PS method during low flow in one instance. The dissolved constituent of TP, SRP, was significantly greater for the PS sampling method during storm flow conditions; for phosphorus concentrations, differences are most likely due to seasonal variability and large differences in observations rather than bias between sample methods. For TN concentrations, our study found it may be underrepresented by the PS method during storm flow conditions. NO_3-N was the only constituent without any significant differences between methods at all flow conditions, which provides evidence that NO_3-N is accurately sampled by the PS method.

Depending on the flow conditions, stream geometry, and study time length, EWI and PS sampling methods both a have a place in acquiring accurate constituent concentration data depending on the needs of the researcher. Beaver Lake is an important and increasingly utilized resource; proper management of the Beaver Lake and its watershed requires accurate knowledge of ongoing land uses and the seasonal factors that contribute nutrient and sediment loading. To increase the utilization of resources, PS sampling methods need be incorporated for appropriately measured constituents in short-term studies, but also for accurately following long-term seasonal variation in sediment and nutrient loading.

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