

Quantifying in-Stream Processes on Phosphorus Export Using an Empirical Approach

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ABSTRACT

In-stream nutrient release and retention control the timing and quantity of export at the watershed outlet by mobilization and transport of phosphorus (P) sources from land to the channel, and remobilization of transient stores of P from stream beds. We investigated the significance of stream processes in regulating P loading to the Cannonsville watershed, NY, USA. A mass balance of estimated P inputs to the stream with observed P export at the watershed outlet was used to quantify P delivery and explore the behavior of P. Stream channel transport of both dissolved and particulate P is found to be non-conservative, with dissolved P being retained during low flows and particulate P released during high flows. The results suggest that differences in the magnitude and relative importance of in-stream biogeochemical processes under different flow regimes regulate P delivery in ways that may influence ecological impacts to downstream river reaches and reservoirs.

KEYWORDS

Point Sources; Non-Point Sources; P Release and Retention; Linear Mixing; E-EMMA

1. Introduction

Phosphorus (P) contamination of surface waters originates from sources such as agriculture, municipal sewage treatment plants, individual septic treatment systems, decaying plant residue, runoff from urban areas and construction sites, stream bank erosion, and wildlife. In the Cannonsville Reservoir watershed, NY, P losses from agriculture are known to be a major source of P entering streams and the reservoir [1]. The downstream ecological impacts of P inputs are heavily dependent on the extent to which they are physically retained and/or chemically and biologically processed (Edwards and Withers, 2007; Withers and Jarvie, 2008). The net effects of the attenuation, retention, and processing of P are usually ignored in watershed management, where the primary focus is source control. In-stream processing of P loads may account for the apparent disconnect between measures im-

plemented to reduce P inputs and improvements in water quality and ecology at watershed scale [2]. In rivers with P retention occurring during low flow conditions, with the P retained in the river bed subsequently transported during storm events. The release of P can occur within or between years [3,4] and can be along the longitudinal continuum of a single basin [5]. In-stream processes under low and intermediate flows may modify quantity, bioavailability, and timing of nutrient delivery in ways that reduce downstream eutrophication risk [6].

Watershed nutrient mass balance estimates require detailed data on topography, land use, soils, watershed management practices, and point source inputs. Total P inputs to the stream channel network are the sum of all the nonpoint and point sources in the watershed. These inputs can then be compared with the P loads at the watershed outlet. Such analysis provides an estimate of net gain and loss. Uncertainties in P, storage and transformation in the stream channel network may add considerable

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uncertainties to P export estimates independent of the uncertainty in watershed inputs [7]. Understanding the ability of streams to accumulate, transform, or release P under differing hydrologic conditions is essential for understanding watershed scale P export to downstream areas [7,8].

In its simplest breakdown, P can be transformed biogeochemically between dissolved phosphorus (DP) and particulate phosphorus (PP) during transport process. The pools of DP and PP are not static in surface water. DP may be taken up by plants, algae, microorganisms or may be bound by minerals or sediment to form PP [2]. Phosphorus readily adsorbs onto particulate matter and is commonly transported in the particulate form. Episodic transports occur during high flow events when inputs of particulates are high and in-stream retention is low [9]. The study by Doyle *et al.*, [10] showed that both low flow and moderate floods maintained the P budget with low flows dominating P retention and moderate floods maintaining the output predominantly as PP. The stream bed sediments act as a sink, accumulating inorganic P from point sources during low flow periods. Discharges at different flow conditions can be expected to have different ecological effects for a given stream and are necessary to maintain long term nutrient balance [11]. The entire range of discharges will influence differing ecological processes, with a certain ecological variable (e.g., nitrate load, periphyton accumulation, phosphorus loads) being most influenced by a particular portion of the hydrologic regime.

Few studies estimate and address the impact of P control measures on in-stream P retention over a range of flow conditions [12]. P retention during spring and early fall and release of stored P during winter were reported by [13] in a study of River Cherwell in Oxfordshire, England. McDowell and Trudgill (2000), in a study of South Devon, England reported that episodic release of P in summer mostly attributed to direct cattle access to stream, increases in soil P in summer from warmer temperatures, and P inputs via fertilizer or effluent spreading. These studies however did not address whether the P concentration were related to DP or PP. Meyer and Likens [8] reported that net P retention was inversely related to discharge, *i.e.*, as discharge increases, less DP was retained in their study reach. Retention of nutrients is of critical importance to the operation of stream ecosystems because the availability of food resources to aquatic organisms is largely determined by the nutrients retained. Retention of dissolved nutrients permits levels of primary production and microbial growth necessary to support grazing invertebrates [14]. Consumers in the upper food chain of streams, such as fish that rely on invertebrates for food are thus dependent on retention processes to supply food resources for their invertebrate

prey. The amount of retention is determined by a complex interaction of valley floor geomorphology, riparian conditions, and in-stream biological demand that accentuates the intimate linkage between aquatic and terrestrial ecosystems.

Understanding the net effects of P release and retention processes in watersheds is important in the interpretation of effective management, remediation, and restoration measures. Such an understanding may also be incorporated in water quality models to improve the magnitude and timing of nutrient predictions. The goals of this study were to analyze in-stream P processes under different flow regimes, and evaluate possible variability due to flow, season, release, and retention processes using data from a number of different events. This analysis could potentially be used to examine the scale and variability of DP and PP retention and release, as an aid to watershed management, and to improvise in-stream processing algorithms in existing water quality models.

2. Methods

2.1. Study Site

The Cannonsville Reservoir Watershed (CRW) is a New York City (NYC) water supply watershed located in the Catskill region of New York State (**Figure 1**). The watershed drains an area of 891 km² above the USGS gauging station (#01423000) at Walton and is predominantly forested (67%), agriculture (23%), and brush lands (6%). The elevation of the watershed ranges from about 300 m near the watershed outlet to about 1100 m near the headwaters. The mean annual precipitation in this region is 1100 mm [15] and mean annual water yield is 601 mm of which 64% is baseflow and 36% surface runoff [16] based on standard hydrograph separation techniques [17].

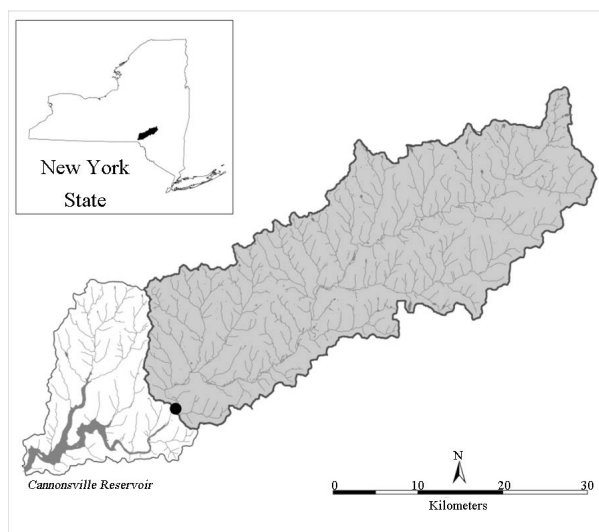


Figure 1. Map of cannonsville reservoir watershed, NY.

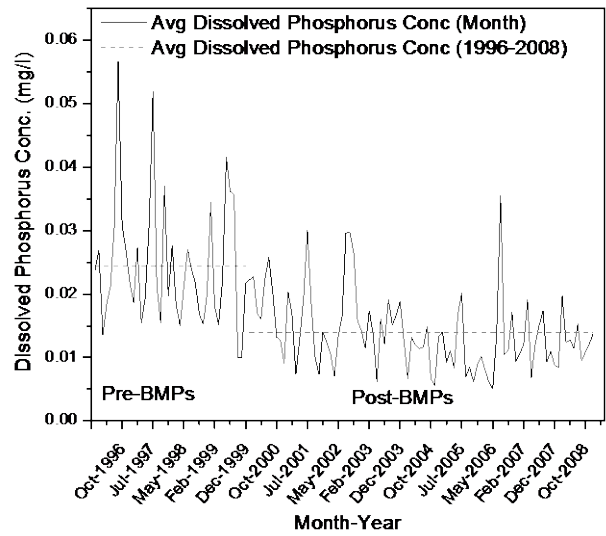
As part of efforts to ensure high water quality in the Cannonsville Reservoir, the New York City Department of Environmental Protection (DEP), in cooperation with other watershed stakeholders, has implemented a number of watershed management programs. The watershed agricultural programs in the CRW include whole farm plans to protect water quality from agricultural pollution, with particular emphasis on waterborne pathogens, nutrients and sediments. The program also helps farmers to keep livestock out of streams while managing their croplands and pasture lands in a manner that reduces stream-side disturbances and other potential impacts. Regulatory upgrade programs for waste water treatment plants (WWTPs) provide for the design and installation of highly advanced state-of-the-art treatment of WWTP effluent. The CRW has eight WWTPs.

There is a long record of water quality data collected at the Beerston, NY site close to CRW outlet with the specific goal of accurately estimating the dissolved and particulate nutrient loads to the Cannonsville Reservoir (Figure 1). Frequent sampling captured the variations in concentration occurring during all major storm events as well as seasonal variations in baseflow concentration (Longabucco and Rafferty, 1998). Figures 2(a) and (b) show time series line plots for DP and PP concentration from 1996 to 2008. For this study, we used 5 years of data to evaluate the effects of P retention and release on the P loads estimated at the watershed outlet; 1997 (before rigorous implementation of watershed level best management programs (BMPs) addressing both point and nonpoint source pollutants), 2001, 2003, 2005 and 2008 (post BMP implementations). These are also the years when cattle data are available. We chose the four post BMP implementation years to evaluate progressive changes in in-stream nutrient retention and release processes. These years also include both a low flow (2001) and a high flow year (2003).

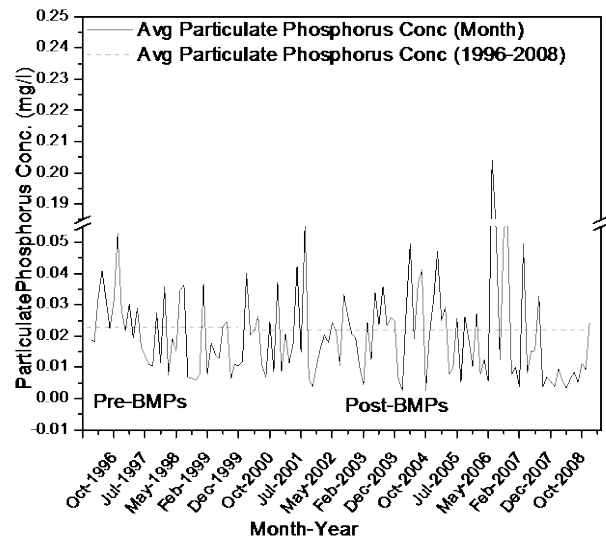
2.2. Mixing Model Analysis

In this study, we adopt a simple empirical approach Extended-End Member Mixing Analysis (E-EMMA) [6,18] (Figure 3) for quantifying P delivery to explore P net retention and release at the watershed outlet. This approach enabled us to utilize water quality monitoring data, and point source data to quantify the impacts of in-stream and watershed P processing on P delivery at the watershed scale. The point source data we used for this study included WWTP effluent nutrient concentrations and estimates of nutrients directly added in-stream by cattle before and after the implementation of watershed management programs that excluded cattle from the stream in CRW.

With E-EMMA, the P load is plotted against flow for two end-member component mixing series. The nutrients



(a)



(b)

Figure 2. Time series of monthly averages of measured (a) DP and (b) PP concentration at Beerston site close to CRW.

considered in this study are DP and PP. The underlying assumption is that there are two dominant and distinct sources of water (both with different P concentrations) contributing to P loads at the watershed outlet: (i) a baseflow end-member source composed largely of point sources such as waste water treatment plant effluents, cattle directly defecating in stream and/or nutrients released from groundwater as sources to stream during these periods, and (ii) an eventflow end-member source composed of a combination of watershed scale nonpoint sources that, under the highest flows, is delivered directly to the watershed outlet. When the two water sources mix, a linear relationship (shown as linear mixing line) between baseflow and eventflow P load end-members would indicate P as behaving conservatively, *i.e.*, P is not

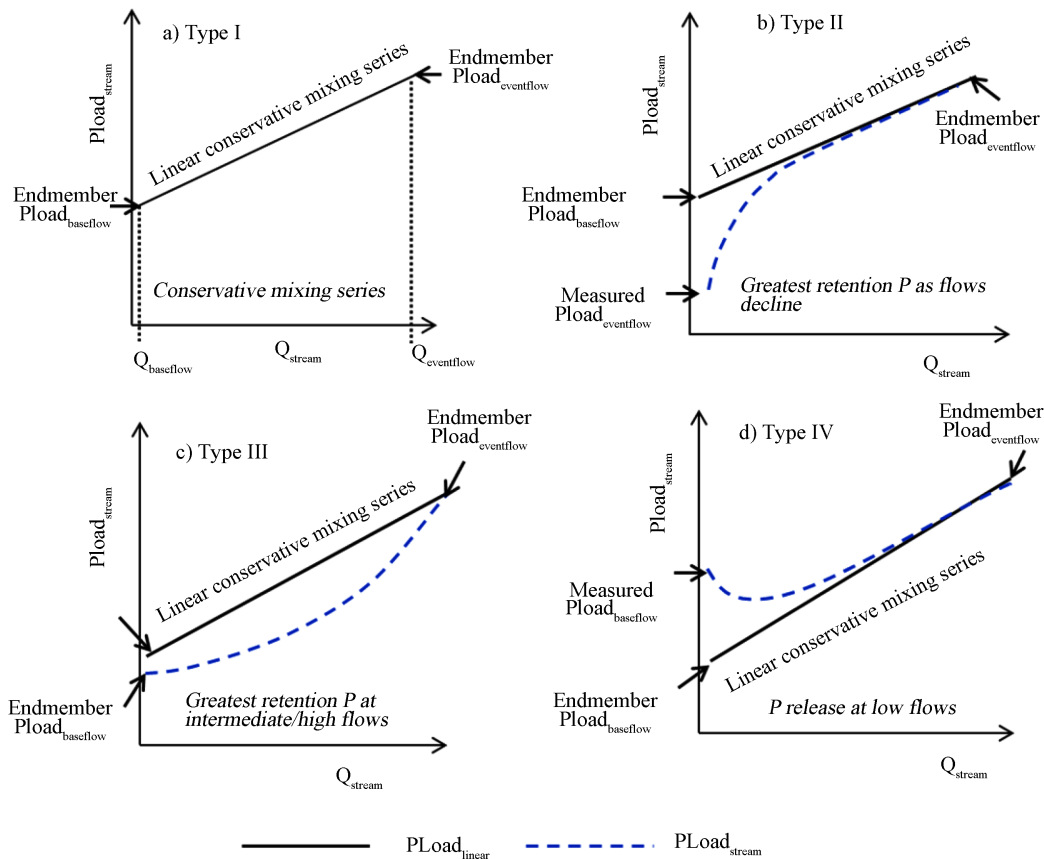


Figure 3. Schematic diagram showing the four main types of relationships between stream P load and stream flow: (a) Type I (conservative mixing series); (b) Type II (Greatest P retention as flows decline); (c) Type III (greatest P retention at intermediate/high flows); (d) Type IV (P release at low flows) (Adapted from Jarvie *et al.*, 2010).

undergoing significant net uptake or release as a result of deposition of PP, remobilization of P, sorption to sediments, or interaction with biota. In contrast, a nonlinear mixing series would indicate that P was behaving non-conservatively. Nonlinear behavior under low-flow conditions is assumed to result from within-stream physical and biogeochemical changes on nutrients resulting in release or retention of nutrients. Nonlinear behavior under intermediate and higher flows represents the net effects of in-stream and watershed retention/mobilization [6]. Under such conditions, P undergoes net uptake or release due to deposition and adsorption to sediments, remobilization of P or utilization by plants, algae or microbes in stream. By comparing an observed nonlinear relationship between stream P load and stream flow measurements, with a theoretical linear conservative mixing series between the baseflow and eventflow end-member P loads, the net effects of P retention and release can be directly quantified.

2.3. Phosphorus Release and Retention Calculation

DP and PP loads for USGS gage (#01423000) at Walton

were used to illustrate how E-EMMA can be used to estimate net losses and gains of P at the watershed outlet. The baseflow end-member P load ($P_{Load_{baseflow}}$) represents the sources of P to the stream that contribute under dry weather flow conditions. “PLoad” is used herein as a standard term to represent either DP or PP. These loads include the sum of the effluents of the eight WWTPs ($P_{Load_{Effluent}}$), direct contributions from cattle in stream ($P_{Load_{Cattle}}$), and any background groundwater sources of P, which in this analysis were considered to be absent (assumptions outlined in Section 2.2):

$$P_{Load_{Baseflow}} = P_{Load_{Effluent}} + P_{Load_{Cattle}} \quad (1)$$

Baseflow P load was calculated each individual year and is assumed to correspond to the lowest ten percentile daily flow value (Q_{10}). This end member was needed to create a linear mixing line as illustrated in Figure 3. The P loads for each upstream WWTP were obtained from DEP and P loads for cattle in stream were calculated based on the animal units, number of hours spent in stream and the manure produced during a day that is dropped directly into the stream. The method for calculating P loads from the cattle in stream can be obtained from James *et al.*, 2008. The eventflow end-member

($PLoad_{Eventflow}$) is an integration of all the watershed-wide sources of P including non-point and point source and P mobilized from within the stream channel network and is estimated for each year from measured rates of P loading:

$$PLoad_{Eventflow} = PLoad_{90th} \quad (2)$$

where, $PLoad_{Eventflow}$ is the stream water P load end member during high flow conditions and $PLoad_{90th}$ is the P load corresponding to the highest tenth percentile daily flow (Q_{90}). So that potential outliers do not skew the end-member calculation, $PLoad_{90th}$ is estimated from a locally weighted smoothing (LOWESS) [19] of the relationship between daily P load at the outlet ($PLoad_{Outlet}$) and daily discharge at the outlet (Q). The LOWESS smoothing used in this analysis is 0.5 with two steps. Given the low water residence times and greatest efficiency of P delivery under highest flows, the impact of P retention on $PLoad_{Eventflow}$ is likely to be relatively low. Therefore, the $PLoad_{Eventflow}$ is taken as the reference point for the integrated watershed eventflow end-member, at which there is no net P retention. The end member values can then be used to derive a line describing $PLoad$ versus Q , with the two end member points

$$(Q_{90}, PLoad_{Eventflow}) \text{ and } (Q_{10}, PLoad_{baseflow}):$$

$$PLoad_{Linear} = (Q_{Outlet} * PLoad_{Gradient}) + PLoad_{Intercept} \quad (3a)$$

$$PLoad_{Gradient} = (PLoad_{Eventflow} - PLoad_{Baseflow}) / (Q_{90} - Q_{10}) \quad (3b)$$

$$PLoad_{Intercept} = PLoad_{Eventflow} - Q_{90} PLoad_{Gradient} \quad (3c)$$

To estimate the net P retention or release, measured values of $PLoad_{Outlet}$ were then compared with the corresponding estimated P load derived from the conservative mixing model ($PLoad_{linear}$) as illustrated by **Figure 3**. Separate values of $PLoad_{Eventflow}$, $PLoad_{Baseflow}$ and the resulting $PLoad_{Linear}$ line are calculated for each year of the analysis. The P load retained or released ($P_{process}$) is calculated for the period of investigation.

$$P_{Process} = \sum_{Period} (PLoad_{Outlet} - PLoad_{Linear}) \quad (4)$$

$P_{Process}$ will be positive during net release and negative for net retention of P by stream processes over the period of interest. In this study, differences in $P_{Process}$ were evaluated for various flow conditions, months and events. Different flow conditions consisted of low-flow conditions (the lowest 10% of flows), high-flow conditions (highest 10% of flows), and for several intermediate flow conditions, *i.e.*, for moist conditions (10% - 40%), one covering mid-range flows (40% - 60%); and another for dry conditions (60% - 90%). The analysis at flow regime scale provides a simple differentiation between P retention/ release as a result of (i) processes that occur under low flows (within the stream or in near-stream environ-

ments) and (ii) wider P processes along the watershed-stream continuum, under intermediate to higher flows. The analysis at the monthly scale helps to highlight any P processes that can be related to land use activities specific to season, while runoff event (constituting a storm hydrograph) scale analysis allows the influence of size, seasonality, and/or dominant runoff processes of the events contributing to release or retention of P in stream to be evaluated.

3. Results and Discussions

For all the five studied years, the relationships between stream P load ($PLoad_{Outlet}$) and streamflow were nonlinear, with none approximating the conservative mixing relationship. Such nonlinear relationships indicate that P processes in stream are non-conservative. **Table 1** presents baseflow and event flow end members and corresponding P loads. Net P retention or release processes quantified by comparing the observed curvilinear $PLoad_{Outlet}$ versus stream flow relationships with corresponding P loads calculated using the corresponding linear mixing model, for each flow regime *i.e.*, low, dry, mid-range, moist and high flows are presented in the following section.

3.1. Dissolved Phosphorus Processes

3.1.1. By Flow Regimes

Comparison of observed annual DP load at the outlet and load derived from conservative mixing showed net retention of DP. At the annual scale, net DP release/retention process (all flow regimes included) ranged from 14% release to greater than 30% retention. During 2008 retention was low and nearly balanced release (**Table 2**). When considering different flow regimes, there was net retention of DP in low, dry, mid-range and moist flow regimes for all the five years, while the high flow regime showed release of DP in all of the years (**Table 3, Figure 4**). **Figure 2(a)** shows the decreasing trend of DP concentration from 1996 to 2008 from measured data. The decreasing trend of DP concentration may be attributed to an overall reduced load as the result of watershed management practices and WWTP improvements, as well as stream channel retention of DP from 1997 to 2008. At high flows DP release varied by years. **Figure 5** shows scatter plots of net differences in DP load for all the years of study. The release process was dominant in moist and high flow regime, with the highest releases occurring during high flow periods. DP was retained at low to mid-range flow regimes and DP retention was greatest under the lowest and intermediate flows, which is strongly indicative of biological processing of P, particularly uptake by algae and/or sorption to sediments. Low flows correspond with highest water residence times

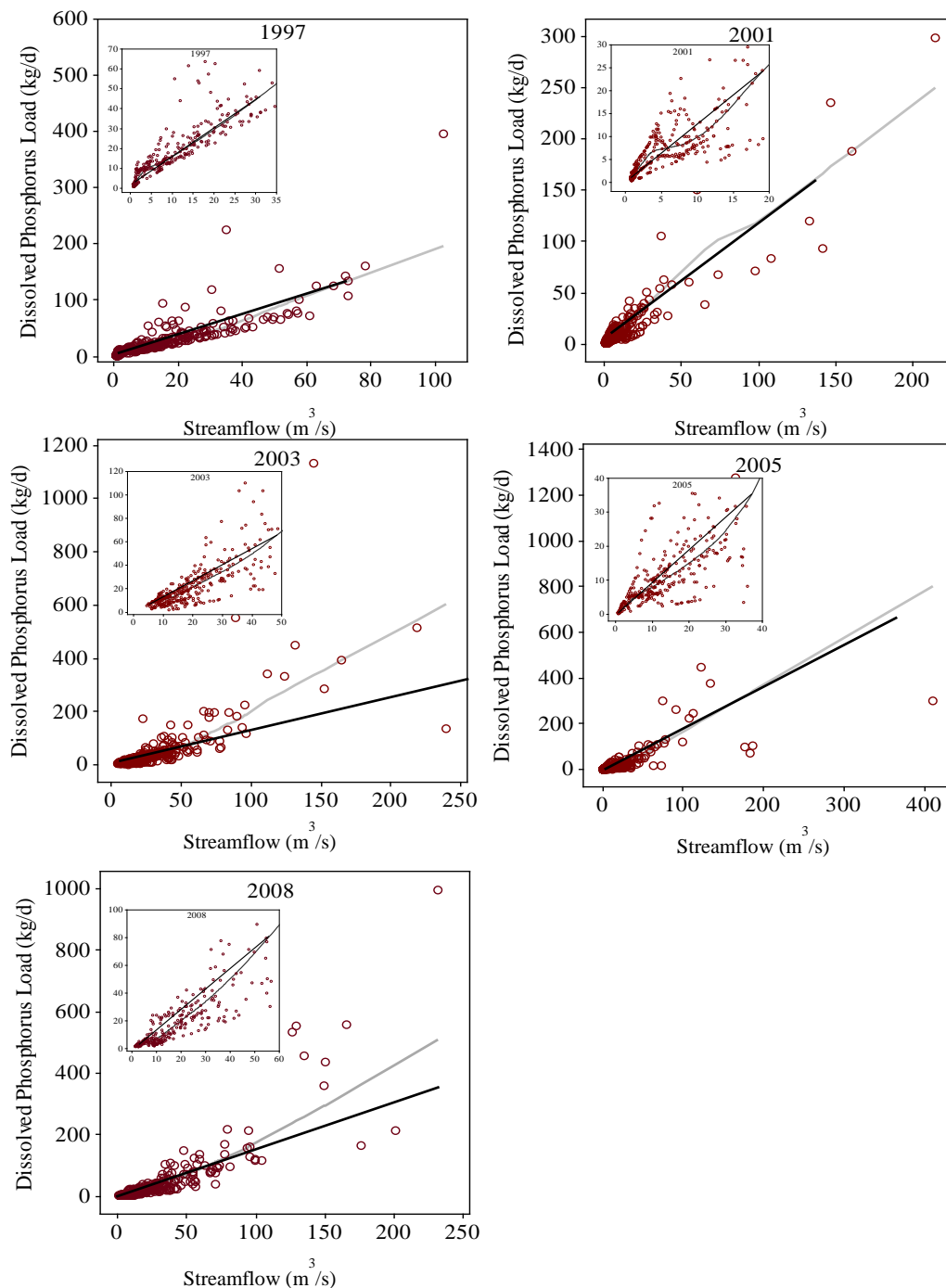


Figure 4. Scatter plots showing non-conservative behaviors of DP. The points show the daily observed P loads and flows, light grey line show the LOWESS smoothed (50%) line through the daily points and the dark lines show the E-EMMA line with the endpoints of $Pload_{baseflow}$ and $Pload_{eventflow}$. Daily points above the E-EMMA line represent P release while points below the line represent P retention. Inset figures are zoomed extent (up to 90th percentile flow and corresponding P load) of curvilinear relationship.

[20] allowing greater interaction with sediments and biota and thus greatest potential for biogeochemical cycling [6]. There is also potential for P retention as a result of an increased proportion of total flow being stored in hyporheic sediments under baseflow conditions. There

was no evidence of significant net release or remobilization DP loads under low and intermediate flows relative to the linear conservative mixing model. This indicates that remobilization of transient in-channel and watershed stores of P was small relative to P load retention under

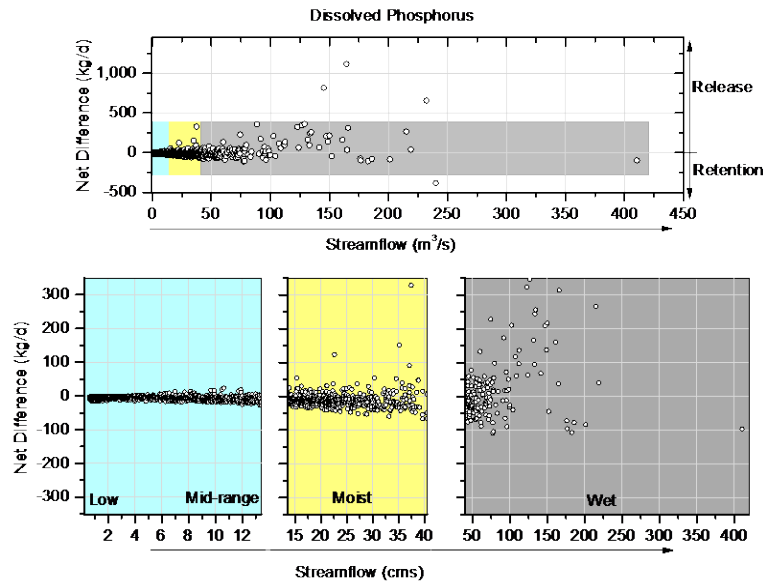


Figure 5. Scatter plots showing conservative behaviors of DP for all five years. The top scatter plot shows streamflow and net difference in P load for all five years. Bottom three plots are zoomed portions of the region highlighted in the top plot. The blue region indicates the low to mid-range flow regimes, the yellow region indicates the moist region, and the grey plot indicates the high flow regime. Points above the zero net difference indicate release of P and points below indicate retention.

Table 1. Baseflow and event flow end members and corresponding P loads. (Note: Loads corresponding to the baseflow end member are from the observed P load. P load corresponding to eventflow end member are loads from LOWESS fit).

Year	End-member	Flow (m ³ /s)	DP load (kg/d)	PP load (kg/d)
1997	Baseflow	0.75	15.26	6.67
	Event Flow	31.05	66.16	69.85
2001	Baseflow	0.65	10.75	3.8
	Event Flow	19.11	24.97	23.6
2003	Baseflow	5.66	13.84	3.8
	Event Flow	48.34	105.88	114.26
2005	Baseflow	0.71	3.22	3.15
	Event Flow	35.32	36.6	252.67
2008	Baseflow	1.58	4.90	2.62
	Event Flow	55.08	83.04	59.89

low and intermediate flows. In-stream processes under low and intermediate flows may therefore reduce delivery and modify the timing of DP loads to the stream outlet.

3.1.2. By Month

In order to further understand P retention and release processes, we analysed the P processes data by month. There was no distinct pattern of the retention or release processes observed on monthly basis, however DP was generally retained in more months than it was released. DP was released during February for 1997, 2001 and 2008, and also during November of 1997 and 2003 (Figure 6). There was one instance during 2008 when

Table 2. Comparison of observed annual stream P loads (kg) and load derived from the conservative mixing analysis. Difference between observed and conservative loads constitute either net loss (retention) or net gain (release).

Year	Retention/ release (kg) (±)	Retention/ release (%)	Retention/ release (%)	
			Dissolved Phosphorus	Particulate Phosphorus
1997	-11.05	-31.9	4.2*	19.2*
2001	-5.92	-33.0	36.01*	260.1*
2003	-17.87	-30.88	28.49*	50.32*
2005	3.01*	14.39*	57.45*	42.42*
2008	-1.39	-3.88	-1.18	-4.66

Table 3. Comparison of observed stream P loads (kg) and loads derived from the conservative mixing analysis at different flow regimes. Table lists percent difference between observed and conservative loads constitute either net loss (retention-negative) or net gain (release-positive).

P Loads (%)	Flow Regime	1997	2001	2003	2005	2008
DP (%)	High	2.5*	286.6*	2.3*	76.1*	38.7*
	Moist	-28.3	-0.2	-40.7	-25.5	-23.2
	Mid-range	-47.1	-30.6	-54.3	-25.7	-47.6
	Dry	-69.3	-78.1	-56.5	-25.2	-54.5
	Low	-90.2	-92.8	-53.3	-84.6	-63.9
P Loads (%)	Flow Regime	1997	2001	2003	2005	2008
PP (%)	High	36.1*	598.6*	132.5*	193.2*	24.8*
	Moist	1.3*	27.0*	17.3*	-79.5	-8.8
	Mid-range	11.1*	-21.7	-23.0	-83.3	-58.2
	Dry	75.3*	-39.8	-40.9	-82.4	-67.4
	Low	2.6*	-64.8	-13.9	-84.8	-65.0

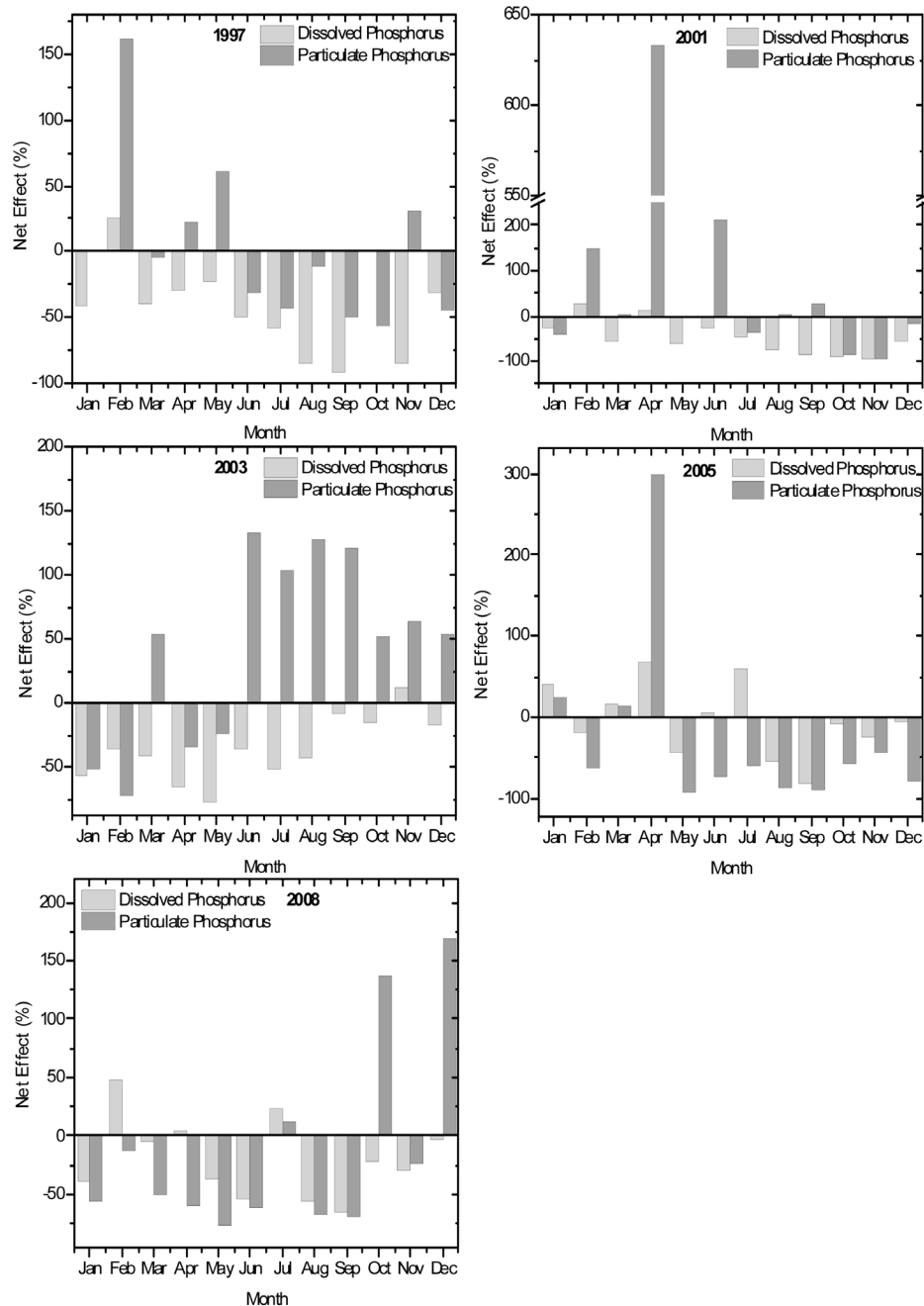


Figure 6. DP and PP processes by month. The negative net differences indicate retention of nutrients and the positive net difference indicate release of corresponding nutrients. These plots are based on daily measurement

unusually high summer streamflow and DP release occurred. Such release may again be due to episodic rain during summer months that resulted in nutrient mixing and release from channel or near stream sources.

Average streamflow during July of 2008 was $14.4 \text{ m}^3/\text{s}$ and the least was during 1997 ($1.5 \text{ m}^3/\text{s}$). DP releases observed during February and November for certain years can be attributed primarily due to large storm events that occurred during those months.

3.2. Particulate Phosphorus Processes

3.2.1. By Flow Regimes

PP processing in stream showed varied results. At an annual scale (all flow regimes included), there was PP retention during 2008 with net annual retention of 4.66% (Table 2). There was net release of PP in 1997, 2001, 2003, and 2005, and ranged from 19% PP in 1997 and greater than 200% release in 2001. The trend graph shown in Figure 2(b) indicates fewer changes in PP from

1996 to 2008. The release of PP may be attributed to extremely high P load associated with high streamflow that was observed during certain high flow events during the studied years. PP stream processing analysis at different flow regimes (Table 3, Figure 7) showed that during 1997 there was a net PP release at all flow rates.

During 2001 and 2003 there was net release at high and moist flow regimes; and during 2005 and 2008 there was PP release only at high flows. Over all years PP release was always occurred during high flow, and PP releases at high flow were always the greatest calculated in any year (Table 3, Figure 8).

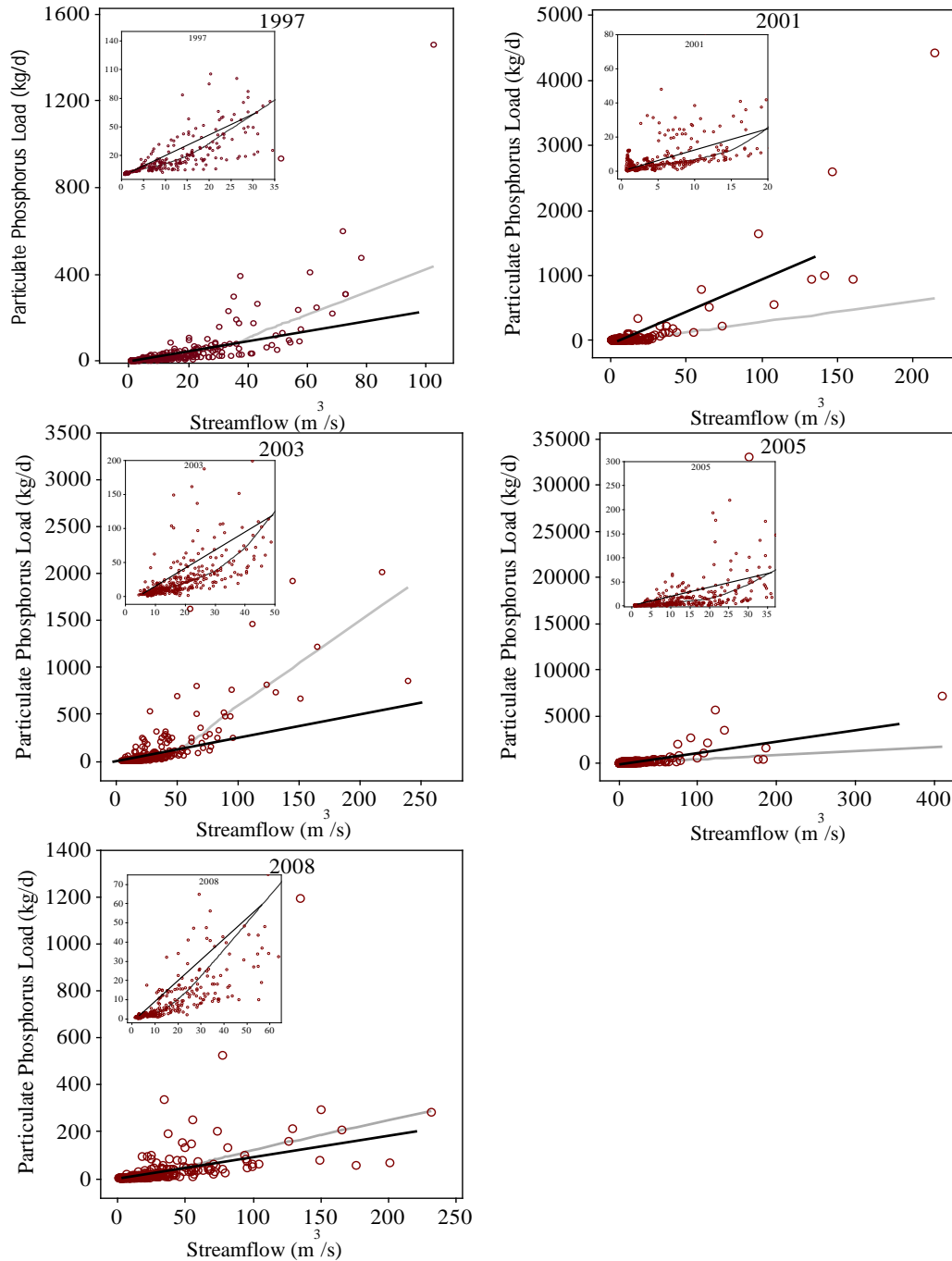


Figure 7. Scatter plots showing non-conservative behaviors of PP. The points show the daily observed P loads and flows, light grey line show the LOWESS smoothed (50%) line through the daily points and the dark lines show the E-EMMA line with the endpoints of $Load_{baseflow}$ and $Load_{eventflow}$. Daily points above the E-EMMA line represent P release while points below the line represent P retention. Inset figures are zoomed extent (up to 90th percentile flow and corresponding P load) of curvilinear relationship.

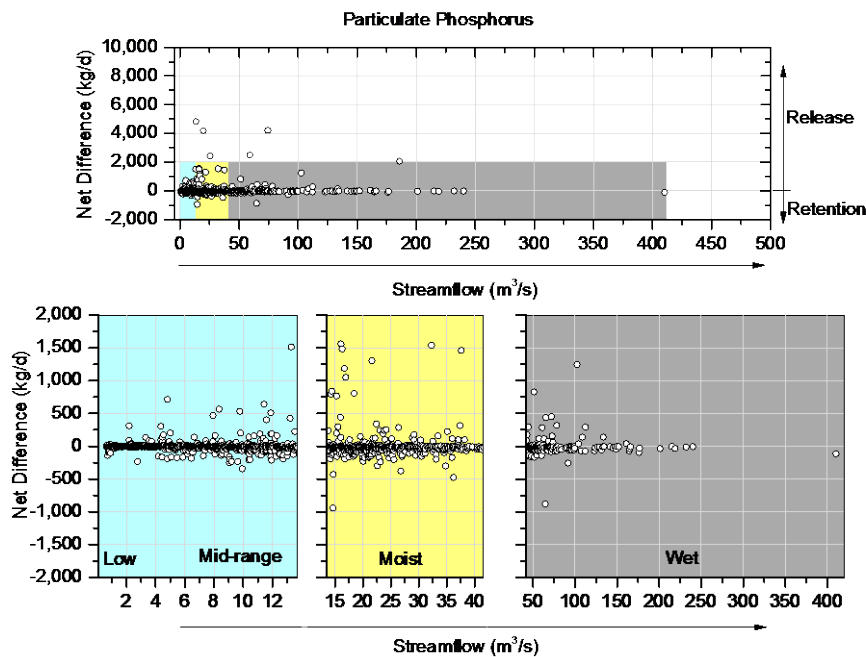


Figure 8. Scatter plots showing conservative behaviors of PP for all five years. The top scatter plot shows streamflow and net difference in P load for all five years. Bottom three plots are zoomed portions of the region highlighted in the top plot. The blue region indicates the low to mid-range flow regimes, the yellow region indicates the moist region, and the grey plot indicates the high flow regime. Points above the zero net difference indicate release of P and points below indicate retention.

P that becomes stored along the stream-watershed continuum (either through physical deposition or by biogeochemical processes such as sorption to sediments or uptake by biota) will subsequently be available for remobilization and thus contribute to the nonpoint-source load (and to the eventflow end-member load) as flows rise [6]. Note that 1997 period was prior to watershed management activities, including many WWTP upgrades and reductions in cattle presence in the stream. It is therefore possible that net release of PP during 1997 at all flow regimes may be due to activities that might have directly contributed P to stream sediments, including the potential sorption of high concentration of wastewater treatment plant effluent and direct contribution of P by cattle in the stream. The greatest release of PP observed during 2005 may be attributed to few high flow events during spring runoff that produced extremely high P loads to the watershed outlet. The greatest net PP retention under low to intermediate flow conditions for 2001, 2003, 2005 and 2008 are likely the result of net deposition of PP along the watershed–stream continuum.

3.2.2. By Month

PP release varied by months and by years (Figure 6). PP release tended to occur during spring and late fall months and these processes are associated with the high flows of this period driven by the combination of snow melt, precipitation events and high antecedent moisture conditions. Our study also showed that events that occurred during

late October and November months resulted in PP release during 1997, 2003 and 2008. The average flow during November ranged from 15.9 m³/s to 54.2 m³/s. An experimental study conducted by Johnson *et al.*, [21] indicated that sediments will release PP and DP when stirred up during storm periods. Their study indicated that particulate forms of P were lost from the watershed almost exclusively during storms and that most of the runoff and P loss occurred in a relatively short time span during which highest discharge rates occurred. Doyle *et al.*, [10] reported from their studies that moderate floods release PP, while retention occurs during low flow conditions.

4. Conclusion

Stream channel transport of both DP and PP is found to be non-conservative, with DP tending to be retained during low flows and PP released during high flows. Our study showed that there was net retention of DP for all the studied years while net release of PP was observed for some years (1997, 2001, and 2003), and that the greatest rates of release were always observed at the highest flow rates. The results suggest that differences in the magnitude and relative importance of in-stream biogeochemical processes under different flow regimes regulate P delivery in ways that may influence ecological impacts to downstream river reaches and reservoirs. In-stream P processing also has implications for understanding the watershed scale effects of management ef-

forts to reduce P loading to streams. Given the well-defined baseflow and eventflow end-members that could be derived from the high resolution Cannonsville P load data, the interpretation here is that the curvilinear relationship (Figures 4 and 7) reflects net P retention along the stream-watershed continuum during mixing of the eventflow and baseflow end members. The use of end member mixing approach to estimate P processing comes with some limitations. The choice of event flow end member can also influence the magnitude of the estimated P processes. Further study is needed to gain fuller understanding of the balance of processes that determine the eventflow end-member load at intermediate to high flow conditions, especially in watersheds dominated by nonpoint export, such as differential erosion associated with events of different magnitudes, intensities, seasons, and pre-existing conditions; re-deposition and other processing active during overland flow; and in-stream processing.

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