

# Watershed discharge modulates relationships between landscape components and nutrient ratios in stream seston

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**Abstract.** In order to understand the environmental controls of the elemental composition of suspended particles in streams and rivers, we examined relationships between the stoichiometry of suspended particles and catchment characteristics (e.g., topography and land cover) under contrasting hydrological conditions in streams from the Upper Peninsula of Michigan, USA. Particulate C:N, N:P, and C:P ratios varied considerably among streams on each of 10 separate sampling dates and within most streams through time. When averaged across the study period by stream, particulate C:N:P ratios were strongly related to several catchment properties. For example, particulate C:P and N:P ratios were negatively related to the percentage of catchment used for agriculture but positively related to the percentage of catchment found as wetlands. These relationships reflected, in part, variable concentrations of mineral particles, which were strongly related to stream length, agriculture, and upstream lake area. In addition, the strength of the relationships between particulate elemental composition and catchment properties changed depending upon hydrologic condition of the Ontonagon watershed. For example, periods of wetness, as indicated by high river discharge, were found to increase the strength of seston C:N ratio–percentage of wetlands relationships but to reduce the strength of seston C:P ratios–percentage of wetlands relationships. Our results thus demonstrate that the balance of elements fluxing through forested streams is strongly affected by catchment properties but that these effects are sensitive to watershed discharge. At times of high discharge, there are strong connections to catchment sources while in-stream processes appear to predominate at time of low discharge.

**Key words:** hydrograph; landscape; sediments; seston; stoichiometry; Upper Peninsula, Michigan, USA; watershed; wetlands.

## INTRODUCTION

The elemental composition of suspended particulate organic matter, hereafter “seston,” has implications for ecosystem processes and food webs in rivers and streams (Frost et al. 2002, Cross et al. 2005). For example, stream seston is an important food source for filter-feeding and collector/gatherer macroinvertebrates in flowing waters (Huryn and Wallace 2000). The quality of this organic matter for filter feeders appears related, in part, to its C:N and C:P ratios (Frost et al. 2002, Cross et al. 2005). In addition, the decomposition rate of stream seston is tied to its N and P content (Cebrian et al. 1998, Cebrian 1999, Cross et al. 2005). At broad scales, seston C:N and C:P ratios will affect the balance of elements exported into downstream ecosystems (e.g., lakes and estuaries; Ebise and Inoue 1991). Consequently, there is a need to understand the environmental

controls of the elemental composition of suspended particles in streams and rivers.

One potential environmental driver of seston elemental composition in streams is the hydrological condition of the upstream watershed. Changes in discharge alter hydrological connections among streams within the drainage network (Thorp et al. 2006, Tetzlaff et al. 2007) and between streams and the surrounding landscape (Tockner et al. 1999, Hein et al. 2003, Pringle 2003), both of which potentially affect the import, processing, and export of dissolved and particulate elements into stream ecosystems. For example, during periods of high flow, increased connectivity between streams and their catchments could result in stronger relationships between seston C:N:P ratios and catchment characteristics that influence the composition of seston particles. Periods of low flow could weaken those linkages, increasing the importance of in-stream production of seston and organic matter processing. The hydrological setting of the watershed thus could be a potentially strong modifier of processes that control the elemental composition of stream particles.

The elemental composition of suspended particles should also reflect features of the landscape that

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contribute, transport, and/or transform C, N, and P moving into and through river ecosystems. For example, a landscape rich in wetlands might increase C:P and C:N ratios of stream seston if wetlands are a significant contributor of N- and/or P-poor particulate organic matter. Alternatively, high C:N and C:P ratios in seston may reflect nutrient limitation of autotrophs and heterotrophs within streams flowing out of wetlands if discharged water has low concentrations of dissolved nutrients (Cross et al. 2005, Frost et al. 2007). In agricultural and other human-dominated landscapes, greater export of sediment-bound or dissolved nutrients (Heathwaite and Johnes 1996, Carpenter et al. 1998, Jarvie et al. 2008) could translate into lower C:N or C:P ratios in seston (Whiles and Dodds 2002). Lakes also could potentially alter stream particle elemental composition by reducing the amount of nutrient-poor allochthonous organic material and increasing the amount of nutrient-rich autochthonous material in outflowing streams (Richardson and Mackay 1991, Cattaneo 1996). In general, the influence of catchment characteristics on particulate elemental composition may occur either by altering the input of particles to streams or by altering in-stream processes that produce and/or transform particulate organic matter (POM). The extent to which hydrological conditions alter the strength and nature of relationships between catchment properties and stream seston remains largely unknown.

Here we examine whether relationships between seston C:N:P ratios and catchment characteristics would be altered by hydrological flow conditions. Our primary objective was to characterize the spatial and seasonal variation in C:N, C:P, and N:P ratios of suspended particles and to relate this variation to landscape characteristics and river discharge. We measured the elemental composition of seston in 35 streams of the Ontonagon River (Michigan, USA) watershed on 10 sampling dates over the course of two consecutive years. We expected strong links between the elemental composition of suspended particles and landscape characteristics known to be sources and sinks of C, N, and P. We further predicted weaker relationships between the landscape and suspended particulate C:N:P ratios during periods of low flow due to a reduced hydrological connectivity between streams and their catchments.

## METHODS

### *Site description*

We sampled 35 streams in the Ontonagon River watershed over the course of two years (2002 and 2003). Streams in this study ranged from small, headwater streams to the main stem of the Ontonagon River. Although sites were nested (i.e., sites located downstream of other sites) due to our single large watershed sampling approach, sites were chosen to ensure a wide and even geographical coverage of the watershed. In a

previous study (Frost et al. 2006), we found no evidence this sampling approach affected the strength or nature of relationships between landscape variables and stream dissolved organic carbon concentrations. The ~3600 km<sup>2</sup> Ontonagon River watershed drains portions of northern Wisconsin (Vilas County) and the Upper Peninsula of Michigan (Gogebic, Houghton, Iron, and Ontonagon Counties). The watershed is predominantly forested and encompasses most of the Ottawa National Forest. Additional details of the geomorphology and landscape that typify the sampled catchments in the Ontonagon basin can be found in Frost et al. (2006) and Larson et al. (2007).

### *Water collection and particulate analysis*

We used a grab sampler at each location to sample water for analysis of seston C, N, and P concentrations. Collected water was placed into acid-rinsed bottles and transported to the laboratory to be processed and filtered within 6 h of collection. Suspended particles were filtered through pre-ashed, pre-weighed, Whatman GF/F filters, dried for 24 h at 60°C, and stored frozen until analysis. Duplicate filters were saved for the analyses of total dry mass, C, N, and P. Total dry mass was determined by reweighing dried filters on a microbalance. We calculated an index of stream mineral particle mass by subtracting the mass of particulate organic carbon from the suspended dry mass. Particulate organic C and N contents were measured using a Costech elemental analyzer (ECS 4010; Costech, Valencia, California, USA). Total particulate P content was measured on a separate set of filters after ashing and persulfate digestion with the molybdate-ascorbic acid method (APHA 1992). Hereafter, we present the molar ratios of the seston C, N, and P with the recognition that our P estimate includes both organic and mineral particulate forms of this element. Unless otherwise noted, all ratios were log<sub>10</sub> transformed before statistical analysis.

### *Landscape analysis*

Catchment characteristics were obtained from previous landscape studies of dissolved organic carbon concentrations in the same streams from the Ontonagon watershed (Frost et al. 2006, Johnston et al. 2008). In general, catchment characteristics were calculated using ESRI ArcView Geographic Information System (Environmental Systems Research Institute, Redlands, California, USA) using landscape data obtained from the National Elevation Dataset Digital Elevation Model (DEM), the National Land Cover Dataset (NLCD) from the U.S. Geological Survey (*available online*),<sup>5</sup> and the U.S. Environmental Protection Agency's Reach File version 3.0 (Dewald and Olsen 1994). The Basin1.avx ArcView Basin Extension (Petras 2000) was used with field locations determined with the global positioning

<sup>5</sup> (<http://edc.usgs.gov/products/landcover/nlcd.html>)

TABLE 1. Summary of landscape characteristics and stream geomorphology of the subcatchments of stream sampling sites in the Ontonagon River watershed, Upper Peninsula, Michigan, USA.

Landscape factor	Abbreviation	Units	Mean	CV	Minimum	Maximum
Stream length	length	km	169	271	1.35	2628
Stream density	strm den	km <sup>-1</sup>	0.75	55.8	0.13	1.95
Mean percentage of slope	slope	%	4.07	34.9	1.33	8.07
Percentage of open water	%water	%	4.04	139	0	22.6
Percentage of upland forest	%upforest	%	70.8	16.8	36.2	92.6
Percentage of development	%dev	%	0.27	286	0	4.32
Percentage of agriculture	%ag	%	5.41	208	0.05	62.8
Percentage of total wetland	%wetland	%	19.1	61.8	0.04	48.2

system to delineate individual catchments for each sample point and to calculate catchment characteristics (e.g., catchment area, mean percentage of slope). The catchment boundaries were used to clip the NLCD data, which were summarized into the following categories for each catchment: percentage of catchment area in wetlands, agriculture, open water, developed, and upland forest. We also calculated total stream length (within the sub-catchment including the tributaries), stream density (total stream length divided by watershed area) and mean slope. Summary statistics show considerable variation among stream catchments for all of the landscape variables included in this study (Table 1). While several of the catchment characteristics were significantly correlated with one another (Table 2), we retained this full set of watershed characteristics due to their individual potential to account for differences in the nutrient budgets of stream ecosystems. For all subsequent statistical analyses, stream length, density, and watershed slope were  $\log_{10}$  transformed and watershed proportions were arcsine-square root transformed.

#### Determination of stream discharge

River discharge data was obtained for one of our sample locations (Middle Branch Ontonagon River, USGS station number 04033000; latitude 46°21'25" N, longitude 89°04'35" W) that is continuously measured by the USGS National Water Information System (*available online*).<sup>6</sup> This gauged station on the Middle Branch of the Ontonagon River is free-flowing and relatively free of upstream water regulation. The discharge at this site is highly correlated to downstream main branches of the river, which are regulated, and to smaller headwater streams higher in the catchment (P. C. Frost, *unpublished data*). We used the mean discharge (in cubic meters per second) over the 24-h period on each sampling date as an index of the hydrological setting of the river network.

#### Data analysis

We initially used a two-way ANOVA to assess the relative effects of sampling site and date on C:N, C:P, and N:P ratios in the suspended particulate matter. We

next calculated the correlation coefficient between each elemental ratio averaged across all dates and each landscape predictor separately. This analysis was followed by a forward stepwise regression analysis of the average of each elemental ratio (C:P, N:P, and C:N) across dates and the full set of watershed characteristics. To further examine whether relationships between seston stoichiometry and catchment characteristics varied through time, we examined the relationships between each elemental ratio and watershed characteristics on each sampling date using forward stepwise regression.

To quantitatively assess the effects of discharge on the relationships between landscape variables and seston C:N:P ratios, we used a multistep regression approach. We first described the relationship between the elemental ratios (C:N, C:P, and N:P) and four of the significant catchment properties (stream length, percentage of water, percentage of agricultural land, percentage of wetlands) on each sampling date (Fig. 1). For each elemental ratio–catchment property regression, we derived a slope, hereafter the slope, for each sampling date. The  $\alpha$  slopes were subsequently related to river discharge, which generated a second set of regression  $\beta$  parameters (Fig. 1). We inferred an effect of discharge on the relationships between landscape predictors and particulate C:N:P ratios if the  $\beta$  slope was found significantly different ( $P < 0.05$ ) from 0. Secondly, we calculated a directional index (DI) by subtracting the absolute value of the predicted  $\alpha$  slope (using the  $\beta$  regression equations) at the lowest discharge from that predicted at the highest discharge. When  $\alpha$  slopes are either all positive or negative, the sign of this difference indicates whether increasing discharge leads to larger absolute  $\alpha$  slopes (positive DI; Fig. 1) and stronger landscape–C:N:P ratio relationships or to smaller absolute  $\alpha$  slopes (negative DI, Fig. 1) and weaker landscape–C:N:P ratio relationships. When there are both positive and negative  $\alpha$  slopes (Fig. 1, line B), the DI could be zero, indicating no change in relationship strength and only a change in the directionality of the relationship. Under this circumstance, we compared the 95% CIs of the predicted  $\alpha$  slopes at highest and lowest discharge. If these intervals overlapped, we concluded that the DI was not significantly different from zero.

<sup>6</sup> (<http://waterdata.usgs.gov/nwis>)

TABLE 2. Correlation coefficients among catchment properties from the Ontonagon watershed.

Property	Strm den	Slope	%water	%dev	%ag	%wetland	%upforest
Length	<b>0.38</b>	0.12	<b>0.49</b>	0.04	0.00	0.04	-0.10
Strm den		<b>0.45</b>	<b>0.43</b>	0.13	0.13	<b>-0.37</b>	0.15
Slope			0.04	0.25	0.07	<b>-0.45</b>	<b>0.46</b>
%water				-0.28	-0.29	0.20	-0.27
%dev					<b>0.58</b>	<b>-0.63</b>	0.10
%ag						<b>-0.68</b>	-0.22
%wetland							<b>-0.46</b>

Notes: Significant correlations ( $P < 0.05$ ) are shown in boldface. For explanations of landscape predictor abbreviations, see Table 1.

We also examined the potential for mineral sediments to explain variability in stream seston C:P stoichiometry. We first related the residual variation around the relationship between seston C and P to the concentrations of stream mineral particles. In addition, we completed the multiple step regression analysis (univariate, stepwise, and  $\beta$  slope regression) as described above using mineral sediment mass as a response variable.

#### RESULTS AND DISCUSSION

We found a wide range in all three elemental ratios when examining data from all sampling dates and locations (Table 3). On average, we found less N and more P in stream seston compared to lake seston as indicated by the lower N:P ratios in stream particles (~15 vs. ~30; Table 3). When the ratios were averaged for each stream through time, particulate C:N ratios were not related to particulate C:P ratios ( $r^2 = 0.02$ ,  $P = 0.36$ ) and weakly related to particulate N:P ratios ( $r^2 =$

0.14,  $P < 0.05$ ). On the other hand, mean particulate C:P and N:P ratios were positively correlated ( $r^2 = 0.66$ ,  $P < 0.01$ ) with one another, indicating a tight coupling of C and N but not P in these streams.

There was considerable within- and among-stream variability in the C:N, C:P, and N:P ratios of suspended particles in these northern Michigan streams. Of the total variation in C:N, C:P, and N:P ratios, a significant and similar percentage was explained by stream sampling site (~25–34%) and date (~18–33%; Table 4). Consequently, variability in particulate C:N, C:P, and N:P ratios in streams of the Ontonagon watershed would seemingly reflect both environmental processes that vary through time (i.e., seasonal changes in discharge or stream attributes such as algal abundance) and features that vary across space (i.e., landscape characteristics that vary among catchments).

When averaged across the study period for each stream, we found strong relationships between the

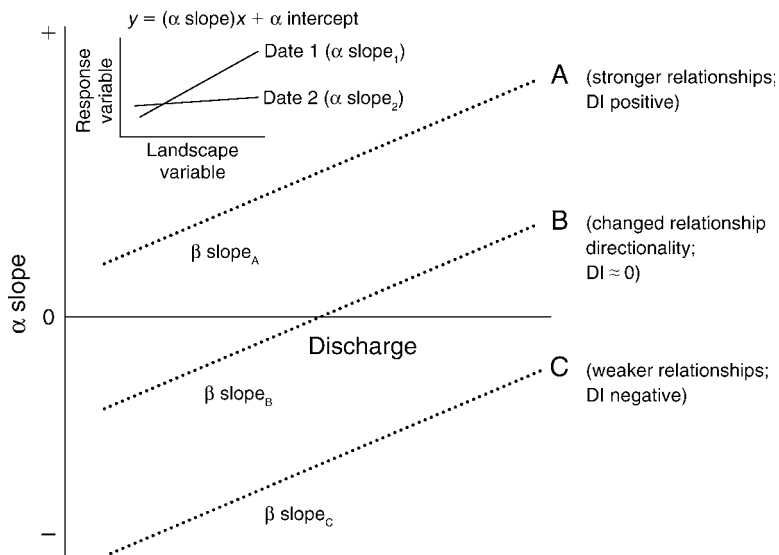


FIG. 1. Potential effects of discharge on relationships between landscape properties and stream seston stoichiometry. The first step of this analysis assesses the relationships between the response variable of interest (e.g., seston C:N ratio) and a landscape predictor (e.g., percentage of wetlands) on each sampling date separately (as in the inset). The resulting set of date-specific slopes (i.e.,  $\alpha$  slopes) are then plotted against the river discharge measured at the time of sampling, which yields a set of  $\beta$  regression parameters. We next ask whether the  $\beta$  slope is significantly different from zero or, in other words, whether discharge significantly alters the slopes between the response and landscape predictor variables. In cases in which the  $\beta$  slope is significantly different from zero, we further determine the relative magnitude and direction of the discharge effect by calculating a direction index (DI).

TABLE 3. Summary statistics for C:N, C:P, and N:P ratios of suspended particulate organic matter in streams from the Ontonagon watershed and freshwater lakes.

Ratio	No. samples	Mean	SD	CV	Minimum	Maximum	Source
Northern Michigan streams							
C:N	333	13.6	4.13	30	6.44	51.6	this study
C:P	332	190.5	95.4	50	49.91	705.6	this study
N:P	332	15.1	8.02	53	2.47	57.06	this study
Freshwater lakes							
C:N	267	10.2	9.0	29			Elser et al. (2000)
C:P	273	307	212	69			Elser et al. (2000)
N:P	267	30.2	15.0	53			Elser et al. (2000)

Note: All ratios are presented on a molar basis.

stoichiometry of suspended particles and particular catchment properties (Table 5). Seston C:N ratios were negatively related to the percentage of the watershed in open water and positively related to percentage of upland forest and catchment slope (Table 5). We also found a relatively weak negative effect of development on particulate C:N ratios. The relationship with open water suggests that upstream lakes are a source of N-rich particles to outflowing streams due to greater autochthonous content of their seston (Voshell and Parker 1985, Cattaneo 1996, Whiles and Dodds 2002). The positive relationships between particulate C:N ratios and percentage of upland forests likely reflect that seston in highly forested streams is composed of more C-rich and N-poor allochthonous organic material, reflecting the greater inputs of terrestrial organic matter in these areas of the watershed (e.g., Fisher and Likens 1972).

Similar to C:N ratios, particulate C:P and N:P ratios averaged for each stream across the study period were strongly related to several catchment properties (Table 5). Using univariate regression analysis, we found seston C:P ratios were positively related to percentage of wetland and negatively related to percentage of development, percentage of agriculture land, and stream length. Forward stepwise regression also showed these relationships with the exception that percentage of development and percentage of wetland were not selected as predictors (Table 5). This is likely due to development and wetlands being highly correlated with agriculture in the Ontonagon watershed (Table 2). With our univariate analysis, we found that seston N:P ratios correlate with a similar set of predictor variables (stream

length, development, agriculture, and wetlands) as seston C:P ratios with the addition of one predictor variable, percentage of water. Of these predictors, stream length, percentage of water, and percentage of wetlands were retained in our forward stepwise regression analysis of stream N:P ratios.

Several explanations, which are not mutually exclusive, could explain these landscape effects on seston C:P and N:P ratios. One explanation for the stream length effect is that suspended algae (of lower C:P ratios) replace allochthonous material (of higher C:P ratios) as the predominant suspended material type in the main branches of the Ontonagon River (Richardson and Mackay 1991, Cattaneo 1996). Another explanation for the P-rich nature of suspended particles in the main branches of the Ontonagon is that longer streams have a greater likelihood of having some agriculture and development in their watershed. Development and agriculture are known for having greater P export rates (David and Gentry 2000, Russell et al. 2008), in part due to the erosion of mineral-rich soils (Howarth et al. 1991, McDowell et al. 2001). The higher particulate C:P ratios in streams containing wetland-rich catchments indicates that wetlands, known for their export of dissolved carbon and retention of other nutrients (Mulholland and Kuenzler 1979, Dillon and Molot 1997, Wetzel 2001), can also alter the balance of elements in particulate organic matter exported to receiving streams.

The negative effects of agriculture and development on particulate C:P and N:P ratios could result from significant inputs of inorganic P associated with suspended mineral sediments in these streams (Meyer and Likens 1979, McDowell et al. 2001). If true, streams

TABLE 4. Two-way ANOVA (var) for the effects of sampling site and date on log(C:N), log(C:P), and log(N:P) ratios in the seston of Ontonagon streams.

Source	df	C:N			C:P			N:P		
		F	P	% var	F	P	% var	F	P	% var
Model	43	13.9	<0.01	67.6	9.50	<0.01	58.7	13.7	<0.01	67.5
Site	34	5.37	<0.01	29.7	8.08	<0.01	39.5	9.41	<0.01	36.5
Date	9	26.0	<0.01	36.4	14.9	<0.01	19.3	30.0	<0.01	30.8
Error				32.5			41.3			33.7

Note: Percentage of variance (% var) was calculated as sum of squares of treatment/total sum of squares.

TABLE 5. Regression relationships between particulate C:N, C:P, and N:P ratios and watershed predictors in the Ontonagon River watershed.

Elemental ratio	Length	Strm den	Slope	%water	%dev	%ag	%wetland	%upforest
Univariate								
log(C:N)	-0.10	0.01	<b>0.41</b>	<b>-0.47</b>	-0.10	-0.11	-0.13	<b>0.51</b>
log(C:P)	<b>-0.43</b>	-0.28	-0.003	0.11	<b>-0.53</b>	<b>-0.55</b>	<b>0.50</b>	-0.05
log(N:P)	-0.29	-0.29	-0.19	<b>0.33</b>	<b>-0.44</b>	<b>-0.47</b>	<b>0.55</b>	-0.29
Sediment mass	<b>0.40</b>	0.24	0.09	-0.28	<b>0.35</b>	<b>0.59</b>	<b>-0.47</b>	0.14
Stepwise								
log(C:N)	n.s.	n.s.	0.19 (0.07)	-0.34 (0.12)	-0.65 (0.12)	n.s.	n.s.	0.12 (0.26)
log(C:P)	-0.07 (0.18)	n.s.	n.s.	n.s.	n.s.	-0.41 (0.31)	n.s.	n.s.
log(N:P)	-0.10 (0.10)	n.s.	n.s.	0.59 (0.19)	n.s.	n.s.	0.34 (0.30)	n.s.
Sediment mass	0.38 (0.16)	n.s.	n.s.	-1.83 (0.14)	n.s.	1.28 (0.35)	n.s.	n.s.

Notes: All elemental ratios and catchment variables were transformed prior to running the regression analysis (see *Methods*). Significant univariate relationships ( $P < 0.05$ ) are shown in boldface. Stepwise regression retained watershed predictors having a  $P < 0.05$ . The partial  $r^2$  of each predictor variable is shown in parentheses; n.s., not selected. For explanations of watershed predictor abbreviations, see Table 1.

receiving a significant quantity of mineral sediments should have lower particulate C:P ratios. Concentrations of suspended mineral particles were found to range widely (0.03–236 mg dry mass/L) among the streams and dates sampled in this study. We detected a significant effect of mineral sediment mass on the residual variation between suspended C and P, with more sediment-rich samples having a lower seston C:P ratio (Fig. 2). In addition, there were significant correlations between stream mineral particle concentrations and certain land use variables (Table 5). Wetlands and lakes were negatively correlated with mineral

sediments, which indicates that these types of land use limit or intercept the export suspended mineral sediments in the Ontonagon watershed. In contrast, stream length, agriculture, and, to a lesser extent, development were positively correlated with stream mineral particle concentrations (Table 5). Streams having significant development and agriculture were thus significant exporters of mineral particles, which lowered the C:P ratios measured in their seston. These streams are, for the most part, found in the northern portion of the Ontonagon watershed and flow into the main branches of the river. This physical proximity of the main branches to these human-influenced streams and the near-absence of wetlands or lakes in these subcatchments likely explain the significant effect of stream length on both mineral sediment mass and suspended C:P and N:P ratios.

Relationships between suspended particulate C:N:P ratios and watershed properties varied considerably through time (Table 6; Appendix A: Tables A1–A3). Models of particulate C:N and N:P–catchment relationships typically explained less variation (i.e., lower average  $r^2$ ) in the summer months (June, July, August, September) than during the spring (April) or late fall (November) (Table 6). A weaker influence of terrestrial watershed properties might be expected during periods of lower flow due to less external material input (Eckhardt and Moore 1990, Cirimo and McDonnell 1997). In addition, the greater biological activity in streams during summer months may increase the in-stream production and transformation of particles, which would potentially disconnect streams from upstream catchment properties (e.g., Mulholland 1992, Edwards et al. 2000, Minshall et al. 2000). In contrast, there were no apparent seasonal trends and relatively more consistency in the  $r^2$  of regression models of C:P ratios when examined on different sampling dates. Although it is unclear why the relationships between landscape properties and elemental ratios involving N (C:N and N:P) ratios would show less consistency

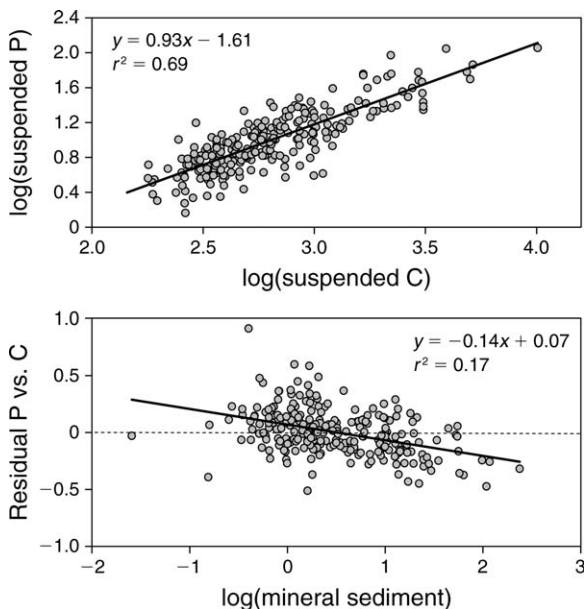


FIG. 2. Relationship between suspended particulate phosphorus and particulate organic carbon in streams and rivers from the Ontonagon watershed. Also shown is the relationship between the residual variation between seston C and P and stream mineral sediment concentrations. Prior to transformation, units for suspended C and P and mineral sediment were in micrograms per liter and milligrams per liter, respectively.

TABLE 6. Stepwise regression between seston C:N, C:P, and N:P ratios and landscape predictors on each date of the study.

Date	Mean discharge (m <sup>3</sup> /s)	Stepwise regression model	r <sup>2</sup>
log(C:N)			
Sep 2002	3.91	+0.33 upforest	0.16
Nov 2002	3.88	+0.16 upforest – 0.56 water + 0.05 length – 0.89 dev + 0.16 slope	0.60
Jan 2003	2.55	–0.27 water + 0.20 upforest	0.35
Apr 2003	10.6	–0.52 water + 0.06 length	0.38
Jun 2003	3.09	–0.55 dev	0.12
Jul 2003	3.20	–0.43 water	0.18
Aug 2003	2.58	+0.51 upforest	0.16
Sep 2003	2.63	none	
Nov 2003	4.21	+0.26 slope – 0.32 water – 0.72 dev	0.44
Apr 2004	9.06	–0.70 water + 0.05 length + 0.12 strm den	0.59
log(C:P)			
Sep 2002	3.91	+0.85 wetland	0.23
Nov 2002	3.88	+0.49 wetland	0.30
Jan 2003	2.55	+0.76 wetland – 0.08 length + 0.39 slope	0.49
Apr 2003	10.6	+0.71 water – 0.08 length	0.33
Jun 2003	3.09	–0.53 ag – 0.51 strm den + 0.43 slope	0.45
Jul 2003	3.20	–0.11 length	0.19
Aug 2003	2.58	–0.59 ag – 0.07 length	0.47
Sep 2003	2.63	–1.22 dev	0.13
Nov 2003	4.21	–1.35 dev – 0.08 length + 0.39 water	0.49
Apr 2004	9.06	–0.08 length + 0.39 water – 0.16 ag	0.53
log(N:P)			
Sep 2002	3.91	+0.50 wetland	0.17
Nov 2002	3.88	+0.48 wetland	0.22
Jan 2003	2.55	+0.67 wetland	0.36
Apr 2003	10.6	+1.22 water – 0.14 length	0.49
Jun 2003	3.09	–0.36 strm den – 0.41 ag	0.36
Jul 2003	3.20	–1.51 dev	0.13
Aug 2003	2.58	none	
Sep 2003	2.63	none	
Nov 2003	4.21	+0.35 wetland + 0.70 water – 0.10 length	0.69
Apr 2004	9.06	+1.00 water – 0.16 length + 0.25 wetland	0.72

Notes: All watershed predictors were transformed prior to each test (see *Methods*), and the mean discharge from the middle branch of the Ontonagon River for the day of sampling is listed. Stepwise regression retained watershed predictors with  $P < 0.05$ . Shown are the slopes, their directionality, and the  $r^2$  of each model. For an explanation of watershed predictor abbreviations, see Table 1.

through time, this result indicates a greater sensitivity of the links between catchment properties and N import (dissolved and particulate) processes to changes in hydrological conditions in streams from the Ontonagon watershed.

As we found qualitative differences in the relationships between catchment characteristics and seston elemental composition among sampling dates (Table 6; Appendix A: Tables 1–3), we next asked whether changes in the hydrologic condition of the watershed could quantitatively explain the differences seen across the study period. To address this question, we developed an analytical approach to assess the effects of discharge on the relationships between suspended C:N:P ratios and key catchment characteristics (Fig. 1). While this analysis is partly constrained by the limited number of sampling events, it nonetheless revealed that watershed discharge can be a significant predictor of the relationships between seston C:N:P ratios and catchment properties. In general, discharge was a good predictor of  $\alpha$  slopes between C:N and C:P ratios and percentage

of agricultural land and percentage of wetland by explaining up to 70–80%  $\alpha$  slope variability. In particular, we found an increased ability of percentage of wetlands to explain between-stream differences in seston C:N ratios during periods of high flow (positive directional index; Fig. 3; Appendix A: Fig. A1). Increasing discharge altered the directionality (from negative to positive) of the relationships between seston C:N ratios and stream length and percentage of agricultural land (Fig. 3). For seston C:P ratios, increasing discharge reduced the strength of relationships with stream length, percentage of agricultural lands, and percentage of wetlands (negative directional index; Fig. 3). Discharge significantly altered the relationship between seston N:P and percentage of water but no other selected watershed characteristic (Fig. 3).

Explanations for discharge-related changes in landscape–elemental ratio relationships would need to consider how the source (internal vs. external) and/or processing of stream particles changes as a function of

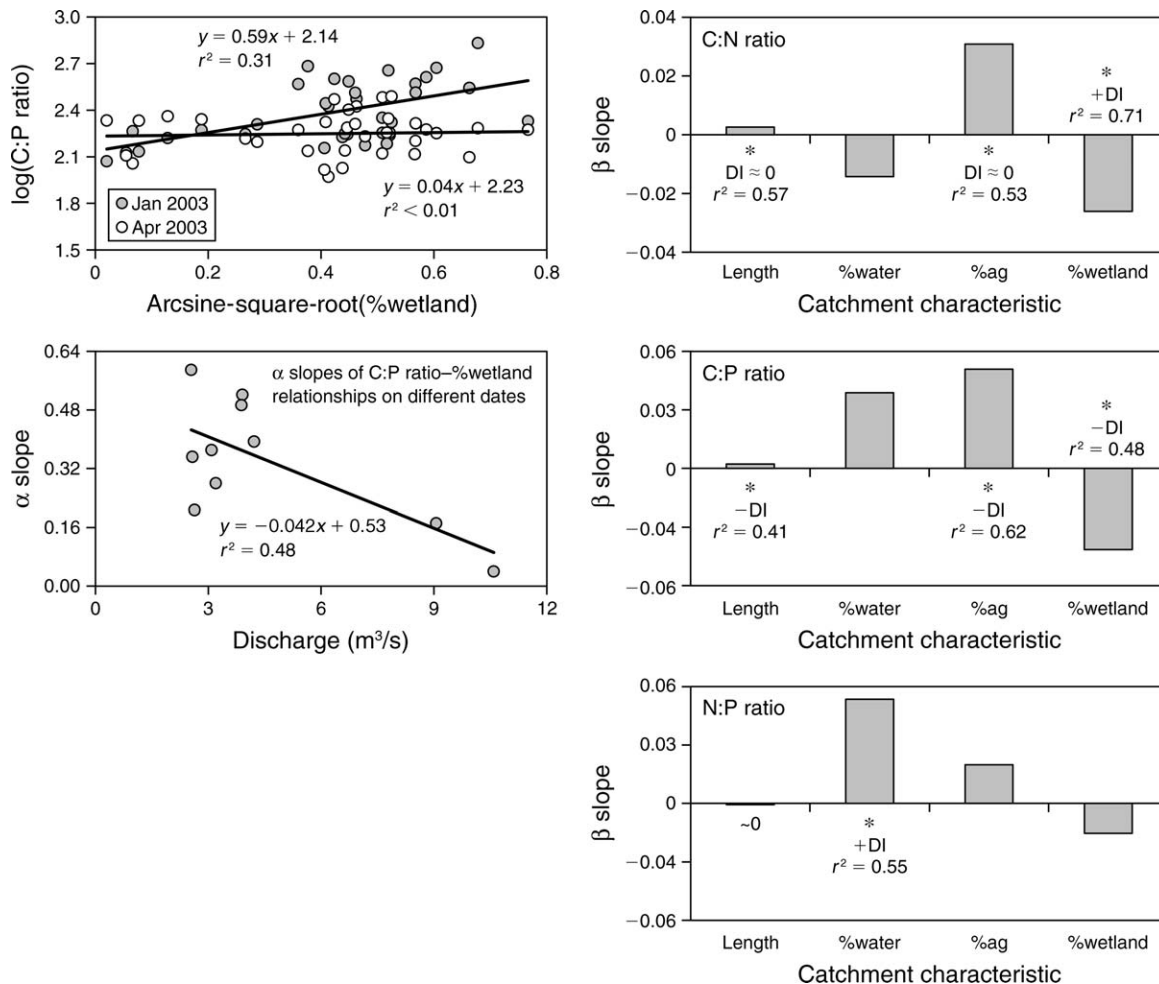


FIG. 3. Example calculations of  $\alpha$  (from two dates) and  $\beta$  slopes (for one elemental ratio–landscape predictor pair). Also shown are  $\beta$  slopes for relationships between discharge and the  $\alpha$  slopes between each elemental ratio (C:N, C:P, and N:P) and four selected catchment characteristics. An asterisk indicates that the  $\beta$  slope was found to be significantly different ( $P < 0.05$ ) from zero. For significant  $\beta$  slopes, we indicate whether the difference index (DI) was positive or negative and show the  $r^2$  of the relationship. For an explanation of landscape predictor abbreviations, see Table 1.

watershed discharge. The pattern of stronger C:N ratio relationships with percentage of wetland under high discharge conditions might be explained, in part, by seasonal differences in the type of particles, having a unique C:N ratio, delivered to the stream from this land cover type. If greater quantities of N-poor particles were delivered from wetland-rich catchments relative to other types of land cover during high discharge periods, then percentage of wetlands would explain more variability in seston C:N ratios during these periods. Alternatively, high discharge periods may correspond to periods of rapid transport and relatively low biological activity (i.e., non-summer months), which might limit the opportunity for internal biogeochemical processing to degrade or modify organic matter. If so, differences in particle C:N ratios among streams having catchments with contrasting land cover may be amplified or

attenuated, depending upon the element, the biogeochemical processes involved, and river discharge.

Increasing watershed discharge was found to weaken landscape–C:P ratio relationships, which was opposite of the discharge effects observed on percentage of wetlands–C:N relationships. This indicates there are distinct biogeochemical processes that control particulate P content and are poorly coupled to processes controlling stream N dynamics. Nonetheless, these processes were found to be sensitive to the hydrological condition of the watershed. The weaker relationships found between seston C:P ratios and percentage of agricultural land and percentage of wetland during wet periods resulted, in part, from lower C:P ratios being found in most streams during periods of high discharge. One explanation for this is that higher rates of biological processes (e.g., primary production and microbial

decomposition) in the summer months elevate C:P ratios in the seston of wetland-rich streams and lower seston C:P ratios in agriculture-rich streams. It thus appears that the relative importance of aquatic processing vs. terrestrial inputs in determining particulate elemental composition is controlled by the discharge regime. More simply, faster flowing and greater volumes of water reduce the effects of internal biogeochemical processes on material fluxes within streams but the net effect depends upon the element (i.e., N vs. P) under consideration (Mulholland et al. 2008).

Our results show that catchment properties can significantly influence the elemental ratios of seston in stream ecosystems. However, the influence of catchment properties on seston elemental composition varied among the elements considered and depended on the discharge regime of the river. Consequently, we found support for taking a broad geographic view of the determinants of the elemental composition of seston but one that incorporates a dynamic response to water fluxes between the landscape and receiving streams. This work provides the basis for additional studies that examine the biogeochemical mechanisms that account for within- and between-stream variation in particulate C:N, C:P, and N:P ratios. These studies would need to examine the landscape contributions of dissolved and particulate nutrients, the importance of internal processing and storage, and include periods of contrasting watershed discharge.

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#### APPENDIX

The relationships between seston C:N:P ratios and landscape variables on each sampling date and in relation to watershed discharge in the Ontonagon River watershed, Upper Peninsula, Michigan, USA (*Ecological Archives* E090-112-A1).