

Effects of lakes and reservoirs on annual river nitrogen, phosphorus, and sediment export in agricultural and forested landscapes

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Abstract:

Recently, effects of lakes and reservoirs on river nutrient export have been incorporated into landscape biogeochemical models. Because annual export varies with precipitation, there is a need to examine the biogeochemical role of lakes and reservoirs over time frames that incorporate interannual variability in precipitation. We examined long-term (~20 years) time series of river export (annual mass yield, *Y*, and flow-weighted mean annual concentration, *C*) for total nitrogen (TN), total phosphorus (TP), and total suspended sediment (TSS) from 54 catchments in Wisconsin, USA. Catchments were classified as small agricultural, large agricultural, and forested by use of a cluster analysis, and these varied in lentic coverage (percentage of catchment lake or reservoir water that was connected to river network). Mean annual export and interannual variability (CV) of export (for both *Y* and *C*) were higher in agricultural catchments relative to forested catchments for TP, TN, and TSS. In both agricultural and forested settings, mean and maximum annual TN yields were lower in the presence of lakes and reservoirs, suggesting lentic denitrification or N burial. There was also evidence of long-term lentic TP and TSS retention, especially when viewed in terms of maximum annual yield, suggesting sedimentation during high loading years. Lentic catchments had lower interannual variability in export. For TP and TSS, interannual variability in mass yield was often >50% higher than interannual variability in water yield, whereas TN variability more closely followed water (discharge) variability. Our results indicate that long-term mass export through rivers depends on interacting terrestrial, aquatic, and meteorological factors in which the presence of lakes and reservoirs can reduce the magnitude of export, stabilize interannual variability in export, as well as introduce export time lags. Copyright © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

Internal biogeochemical processes in lakes, and to a lesser degree in reservoirs, have been key subjects of limnological research for decades (Wetzel, 2001). However, the effect of these lentic ecosystems on riverine transport remains an emerging research frontier. Meanwhile, remote techniques have recently helped refine the global census of water bodies, revealing a larger number of lentic systems than previously thought, including numerous artificial water bodies in agricultural landscapes (Downing, 2010). Thus, many lentic ecosystems are positioned to intercept polluted continental runoff, perhaps to the benefit of downstream ecosystems and biota.

The incorporation of lakes and reservoirs into landscape models has revealed important contributions of

these ecosystems to global biogeochemical cycles. For example, lakes and reservoirs can contribute substantially to river network nitrogen retention (Wollheim *et al.*, 2008; Harrison *et al.*, 2009) and carbon burial or gas emission (Cole *et al.*, 2007; Bastviken *et al.*, 2011). For intensively cultivated landscapes of the Midwestern US, reservoirs can be sinks for nitrogen (David *et al.*, 2006) and phosphorus (Smith *et al.*, 1997; Bosch and Allan, 2008; Brown *et al.*, 2011; Robertson and Saad, 2011), reducing deliveries to downstream ecosystems. Typically, effects of lakes and reservoirs within river networks have been expressed as changes in flux magnitude, but changes in flux variability may also occur. This has recently been shown through decreased intra-annual variability of stream dissolved organic carbon fluxes downstream of natural lakes (Goodman *et al.*, 2011). Overall, it is apparent that the influence of lentic ecosystems on downstream chemistry extends to a wide range of landscape types (e.g. Kelly, 2001; Brown *et al.*, 2008) and pollution forms, including excess nutrients responsible for eutrophication

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of aquatic ecosystems (Vitousek *et al.*, 1997; Carpenter *et al.*, 1998).

Numerous watershed comparison studies have shown how stream mass transport is affected by landscape features (e.g. Caraco and Cole, 1999; e.g. Jones *et al.*, 2001; Gergel *et al.*, 2002). However, most watershed comparison studies have involved time frames of a few years or less (but see Robertson and Saad, 2011). That is problematic because annual mass transport varies substantially with annual precipitation (Alexander *et al.*, 1996; Goolsby and Battaglin, 2001), and transport responses to precipitation are not uniform across landscapes (e.g. Martin *et al.*, 2004). Further, there is a need for improved understanding of how lentic biogeochemical processes vary over longer time frames that incorporate precipitation variability.

Deliveries of excess nutrients and sediment from nonpoint and point sources have caused widespread impairment of United States waters (Howarth *et al.*, 1996; Smith *et al.*, 1997; USEPA, 2012). In the Midwest United States, high river export of nitrogen (N) has been attributed primarily to an increase in the application of N fertilizers (Goolsby and Battaglin, 2001; Turner and Rabalais, 2003; Robertson and Saad, 2011), whereas phosphorus (P) export has been attributed to a combination of fertilizers, manure, and point sources (Robertson and Saad, 2011). Increased soil losses have been linked to both historic (Knox, 2006) and recent (Walling, 1990) land use practices, although soil conservation efforts and reservoir retention have reduced sediment transport in some rivers (Vorosmarty *et al.*, 2003; Renwick *et al.*, 2005). But it remains to be shown how lentic ecosystems differentially affect transport of nitrogen, phosphorus, and sediment through rivers over the long-term.

In this work, we examined the magnitude and interannual variability of total nitrogen (TN), total phosphorus (TP), and total suspended sediment (TSS) across broad gradients of reservoir and lake coverage in contrasting agricultural and forested landscapes. To do so, we used long-term records of annual discharge and mass export for rural catchments in Wisconsin, USA that lack major point sources of nutrients. Our approach focused on the magnitude (mean annual, maximum annual, minimum annual), and interannual variability (as quantified by the CV) of mass export. We expected that the magnitude of export (mass yield as well as flow-weighted concentration) would be higher in the presence of cropland, which has been shown for nutrients and sediment in numerous cases (e.g. Johnson *et al.*, 1997; Liu *et al.*, 2000; Jones *et al.*, 2001). We also expected that retention and removal by lakes and reservoirs would reduce the magnitude of export through rivers, while annual deviations in such processes could affect export variability. For instance, lentic ecosystems might decrease interannual variability in export by functioning

as sinks during years of high flows and loading, though to our knowledge this has not been tested over the long-term for multiple constituents. We therefore used comparisons across catchments and constituent forms to better understand the broad scale effects of lentic ecosystems on the long-term movement of nutrients and sediment in varying landscapes.

METHODS

Wisconsin contains heterogeneous terrestrial and aquatic features associated with varying land practices and past glaciation. This includes a broad gradient of agricultural intensity and abundant lakes and reservoirs that are directly connected to the river network. We used this heterogeneous region to conduct a comparative study of river export across contrasting catchments.

Continuous records of daily discharge and less frequently sampled TN, TP, and TSS have been measured by the US Geological Survey and Wisconsin Department of Natural Resources at river sites throughout Wisconsin. Sites having sufficient discharge and water quality information were examined for long-term patterns in discharge and mass export. We focused on small and intermediate-sized catchments in the range of 100–6000 km² drained by second-order to fourth-order rivers. Sites ranged in latitude from 42.51° to 46.68°N.

Estimation of annual discharge and mass export

Metrics and notation are shown in Table I. We estimated annual river discharge (reported as water yield, m yr⁻¹) and mass export (loads) from relationships between daily concentration and daily discharge. Sites with sufficient information for load estimation were selected by use of the screening criteria of Saad *et al.* (2011). A minimum of 25 non-censored water samples, but more commonly >50 samples, were collected at each site through monitoring programs beginning in 1971. Our analysis focused on load estimates for sites that had at least 10 years of record between 1986 and 2006, which follows a phase of possible stream/river water quality improvement associated with the USA Clean Water Act of 1972. All but two sites had ≥18 years of data. To focus on rural, nonpoint sources of TN, TP, and TSS, we restricted the analysis to sites that had <10% urban coverage in the catchment. In addition, a small number of sites near wastewater treatment outflows or a short distance downstream of another site were also discarded. A total of 54 sites remained for our analysis (Figure 1), with slightly fewer sites available for TN and TP than TSS (TN, *n* = 40 sites; TP, *n* = 46 sites; TSS, *n* = 52 sites). With the exception of a minority of paired sites that occurred on either side (upstream/downstream) of a lake or reservoir, no two sites shared >50% contributing area (most

Table I. Metrics, notation, and data sources

Metric category	Symbol	Units	Description	Source
Landscape features	A	km ²	Catchment area	Calculated from geospatial data ^a
	P_{crop}	%	Percentage catchment area as cropland	Calculated from geospatial data ^b
	P_{lake}	%	Percentage catchment area as lakes or ponds, excluding isolated/disconnected water bodies	Calculated from geospatial data ^c
	P_{res}	%	Percentage catchment area as reservoirs or flowages, excluding isolated/disconnected water bodies	Calculated from geospatial data ^c
Annual export variables	P_{water}	%	Percentage lentic water	$P_{water} = P_{lake} + P_{res}$
	Q_t	m yr ⁻¹	Annual water yield at site i in year t	$Q_t = \sum q_t/A$, q_t =daily discharge
	L_t	kg yr ⁻¹	Annual mass loading at site i in year t	$L_t = \sum l_t$, l_t =daily load
	Y_t	kg km ⁻² yr ⁻¹	Annual mass yield at site i in year t	$Y_t = L_t / A$
	C_t	mg l ⁻¹	Annual flow-weighted concentration at site x in year t	$C_t = L_t / Q_t$
Long-term export variables	Q_{mean}	m yr ⁻¹	Mean annual water yield at site i	Mean Q_t
	Y_{mean}	kg km ⁻² yr ⁻¹	Mean annual mass yield at site i	Mean Y_t
	C_{mean}	mg l ⁻¹	Mean of flow-weighted mean annual concentration at site i	Mean C_t
	Q_{max}	m yr ⁻¹	Max annual water yield at site i	Max Q_t
	Q_{min}	m yr ⁻¹	Min annual water yield at site i	Min Q_t
	Y_{max}	kg km ⁻² yr ⁻¹	Max annual mass yield at site i	Max Y_t
	Y_{min}	kg km ⁻² yr ⁻¹	Min annual mass yield at site i	Min Y_t
	CV_Q	Unitless	Coefficient of variation (CV) for annual water yield at site i	CV of Q_t
	CV_Y	Unitless	CV for annual mass yield at site i	CV of Y_t
	CV_C	Unitless	CV for annual flow-weighted concentration at site i	CV of C_t
R	% yr ⁻¹	Mean mass retention as a percentage of input	Mean of $100*(Y_{in} - Y_{out}) / Y_{in}$	

^a National Elevation Dataset (NED 90 m) and National Hydrography Dataset (NHD).

^b National land cover dataset, 2001 [Homer *et al.*, 2007].

^c 24 K Hydro Geodatabase [WDNR 2009].

sites were independent, and most exceptions shared <20% contributing area). For each site, daily discharge values (q_t , m³ day⁻¹) were summed over each water year (Oct 1–Sep 30) from 1986 to 2006 to estimate annual water yield ($Q_t = \sum q_t/A$, m yr⁻¹, where A is catchment area). Annual TP, TN, and TSS loads (L_t , kg yr⁻¹) for each monitored site were computed with a rating curve/regression procedure in the Fluxmaster computer program (Schwarz *et al.*, 2006) (Appendix A). Annual mass yield ($Y_t = L_t/A$, kg km⁻² yr⁻¹) and flow-weighted mean annual concentration ($C_t = L_t/Q_t$, mg l⁻¹) were calculated. For each site, mean annual Q_t , Y_t , and C_t (Q_{mean} , Y_{mean} , C_{mean}) and interannual coefficients of variation (CV_Q , CV_Y , CV_C) were calculated. Maximum annual yield (Y_{max}) and minimum annual yield (Y_{min}) were also identified. Because the emphasis of this work was to examine the dynamics of river mass export, not effects of changing land use or management, we used linearly detrended (to the long-term median) Y_t and C_t time series in the above calculations. For each constituent form, a minority of sites showed significant linear trends in Y_t (three to five sites) or C_t (17 sites, with

only eight sites showing changes >50% from initial conditions for any constituent) (Appendix Table A1). No site showed a significant long-term linear trend in Q_t .

Catchment land-cover characterization

Catchment boundaries for each site were delineated in Arcmap 10 using the National Hydrography Dataset (NHD) and 90-m National Elevation Dataset (NED). Catchment area (A , km²) was calculated. Percentage of catchment area occupied by row crops (P_{crop}), herbaceous wetland ($P_{wetland}$), forest (P_{forest}), grass/pasture (P_{grass}), and urban (P_{urban}) land-cover classes were calculated from the 2001 National Land Cover Dataset (NLCD 2001, Homer *et al.*, 2007). The Wisconsin Hydrography Database (WHD; WDNR, 2009) was used to identify lakes and reservoirs intersecting the NHD (and thus were directly connected to the river network). We then calculated the percentage of catchment area occupied by connected water bodies, including those classified in the WHD as lakes/ponds (P_{lake}) or reservoirs/flowages (P_{res}).

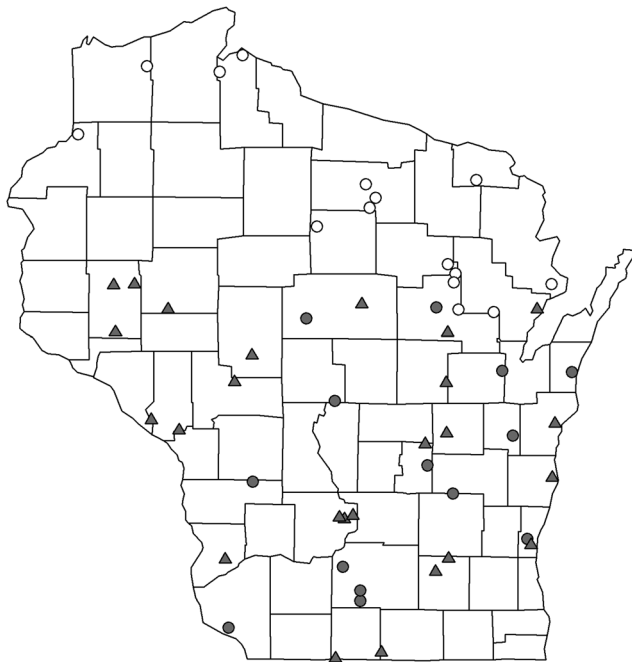


Figure 1. Spatial distribution of Wisconsin long-term river sampling sites ($n=54$). Key (consistent in other figures): white circles = forested catchments (*FOR*), gray circles = small ($<1000 \text{ km}^2$) agricultural catchments (*AG_{small}*), gray triangles = large ($>1000 \text{ km}^2$) agricultural catchments (*AG_{large}*)

A reservoir/flowage is defined as an open water feature that is either labeled as such on a maps, or else has a dam, lock, sluice gate, or other structure controlling its water level (WDNR, 2009). In addition, the total percentage of connected lentic water was computed ($P_{water} = P_{lake} + P_{res}$).

Analysis and statistics

Catchment classes were defined by gradients of agricultural land use (percent cropland, P_{crop}) and size (catchment area, A) using k-means clustering analysis. P_{crop} and A were chosen to define catchment classes because, independent of lakes and reservoirs, the magnitude of export would be expected to increase with P_{crop} , while variability might decrease with A (Alexander *et al.*, 1996). The number of clusters was chosen using a conservative interpretation of the Scree plot (sum of squares (SS) within groups vs number of clusters). Cross-correlation plots for other land-cover classes were examined for covariance (Appendix C) to facilitate interpretation of landscape contrasts.

We compared the magnitude and variability of long-term mass export among catchment classes, and examined lake and reservoir effects within catchment classes. Differences among catchment classes in the magnitude of Q_{mean} , and TN, TP, and TSS export (Y_{mean} , C_{mean}) were evaluated with non-parametric one-way ANOVA (Kruskal–Wallis (KW) test); interannual variability (CV_Q , CV_Y , CV_C) was examined equivalently with KW.

Multiple pairwise comparisons were examined by use of the `pairw.kw` function in the platform R, which uses a conservative method based on Bonferroni correction (Kutner *et al.*, 2005). Within catchment classes, relationships between yield magnitude (Y_{mean} , Y_{max} , Y_{min}) and lentic variables (\log_{10} of P_{lake} , P_{res} , P_{water}), potentially indicating sinks/sources in lentic ecosystems, were examined with regression (model form $y_i = b_1 * \log_{10} x_i + b_0$). To determine if lentic ecosystems reduce interannual variability of river export, we also examined relationships between lentic variables and yield variability with regression. For this, we quantified variability using $CV_Y - CV_Q$ (the difference between mass variability and discharge variability) to isolate effects of lakes and reservoirs on river mass export that are not only driven by discharge variability (CV_Q). To evaluate possible effects of wetlands on river nitrogen (e.g. Jordan *et al.*, 2011), we examined the relation between Y_{mean} and $\log_{10} P_{wetland}$ with linear regression.

Significant negative relationships between yields and the percentage of lentic water ($\log_{10} P_{water}$) provide a basis for estimating retention/loss (hereafter retention) in lakes and reservoirs. When these relationships were significant, retention as a percent of inputs (R) was calculated for each catchment i from $R_i = 100 \times (Y_{in} - Y_{out,i}) / Y_{in}$, where $Y_{out,i} = Y_{mean,i}$, and Y_{in} is a prediction of mean inputs. Y_{in} was estimated from the regression prediction at the lowest value of P_{water} in the regression data. This procedure is based on an assumption that for catchments with otherwise similar landscape features (i.e. similar P_{crop}), the output from catchments deficient in P_{water} serves as a reasonable approximation of the input to lakes and reservoirs of the other catchments. We then calculated maximum annual retention in the same fashion, from significant relationships between Y_{max} and $\log_{10} P_{water}$, which provides a representation of lentic retention during high loading years. R values are reported as averages for each catchment class. Statistical significance is defined as $p \leq 0.05$, and $p \leq 0.10$ is marginally significant.

RESULTS

Catchment characteristics and classification

There was a broad gradient of agricultural land use across catchments. Catchment area (A) ranged from 120 to 5800 km^2 and percentage of cropland in catchment (P_{crop}) ranged from 0.15 to 68% (Figure 2). k-means clustering analysis on $P_{crop} \times A$ indicated three distinct catchment classes ($SS_{BETWEEN \text{ GROUPS}} = 69.6$, $SS_{WITHIN \text{ GROUPS}} = 32.4$). Catchment classes were: low cropland, which corresponded to high forest coverage (*FOR*, P_{crop} range 0.15–11%, A range 180–4000 km^2); high cropland, with small catchment area (*AG_{small}*, P_{crop} range 16–68%,

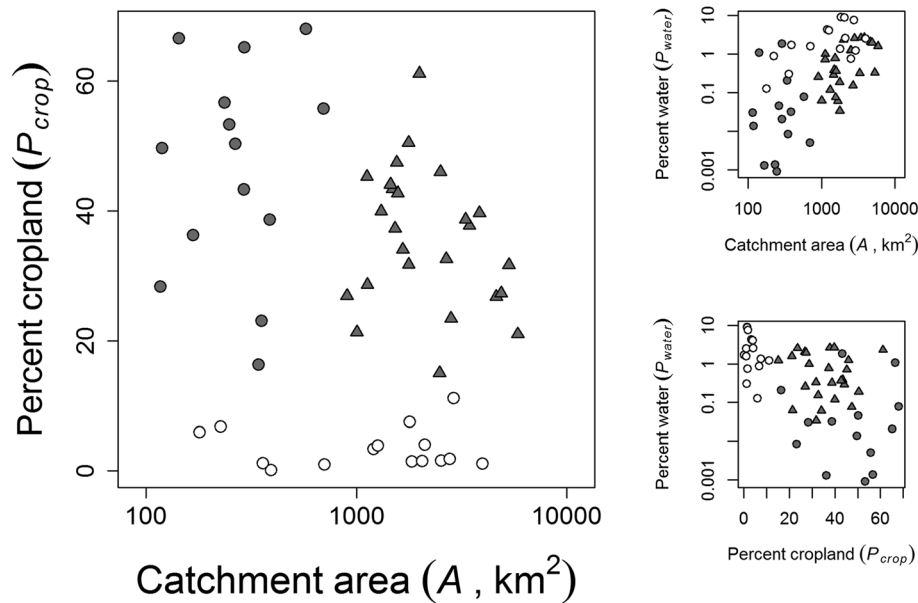


Figure 2. Contrasts in catchment composition for long-term river sampling sites. Catchments were classified by size (catchment area, A) and cropland coverage (percent catchment area as cropland, P_{crop}) by use of a cluster analysis. Differences in coverage by surface water bodies (percent catchment as lentic water, P_{water}) are also shown. Key: white circles = forested catchments (FOR), gray circles = small ($<1000 \text{ km}^2$) agricultural catchments (AG_{small}), gray triangles = large ($>1000 \text{ km}^2$) agricultural catchments (AG_{large})

A range 120–690 km^2); high cropland, with large catchment area (AG_{large} , P_{crop} range 15.0–61%, A range 900–8000 km^2). An alternative catchment classification (four clusters), split FOR into two different groups by larger/smaller catchment area ($SS_{BETWEEN \text{ GROUPS}}=81.3$, $SS_{WITHIN \text{ GROUPS}}=20.7$) but was uninformative for some statistical comparisons due to the low number of monitored small forested catchments. We chose the more conservative catchment classification (three clusters) for analysis, which also had a more balanced representation across classes. FOR catchments were primarily in the northern portion of the study area, while AG_{small} and AG_{large} catchments were relatively dispersed throughout the southern portion (Figure 1). Time series of annual

river TP yield (the basis for analyses below) are shown in Figure 3 for example sites from each catchment class.

There was a broad gradient of lentic water across catchments, with total lentic water as a percentage of catchment area (P_{water}) ranging from 0.001 to 9.0%. Lentic ecosystems in FOR catchments were dominated by lakes (Table II; mean $P_{lake}=2.1\%$, range = 0.30–6.7%; mean $P_{res}=0.96\%$, range = 0.0074–2.3%), whereas a mixture of lakes and reservoirs was present in AG_{small} catchments (mean $P_{lake}=0.19\%$, range = 0.0010–1.8%; mean $P_{res}=0.050\%$, range = 0.001–0.58%) and AG_{large} catchments (mean $P_{lake}=0.51\%$, range = 0.014–1.3%; mean $P_{res}=0.43\%$, range = 0.020–1.5%). When examined across catchment classes, $\log_{10} P_{water}$ and $\log_{10} A$

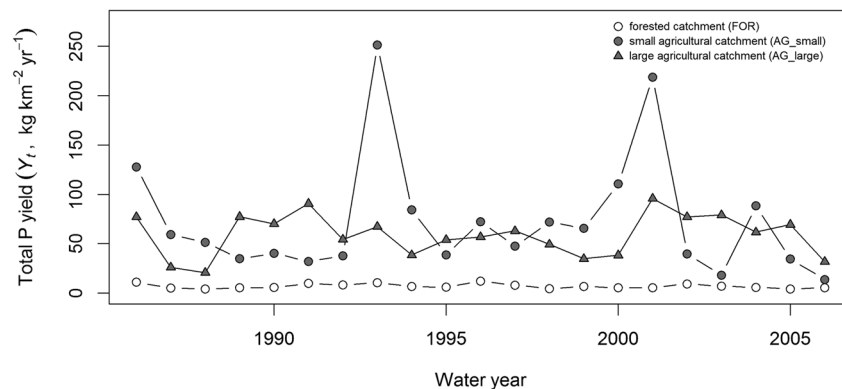


Figure 3. Example time series of total phosphorus yield for three catchment classes used in the analysis. Sites are: forested (FOR , white circles), Popple River near Fence, WI (Site = 4063700, catchment area (A) = 360 km^2); small agricultural (AG_{small} , dark circles), Black Earth Creek at Black Earth, WI (Site = 5406500, A = 120 km^2); large agricultural (AG_{large} , dark triangles), Hay River at Wheeler, WI (Site = 5368000, A = 1100 km^2)

Table II. Mean attributes of sites within the three catchment classes^a

Variable	Catchment class			
	<i>FOR</i>	<i>AG_{small}</i>	<i>AG_{large}</i>	
<i>n</i>	15	14	25	
Catchment area, <i>A</i> (km ²)	1700	340	2500	
Total lentic water, <i>P_{water}</i> (% of <i>A</i>)	3.1	0.24	0.94	
Lake water, <i>P_{lake}</i> (% of <i>A</i>)	2.1	0.19	0.51	
Reservoir water, <i>P_{res}</i> (% of <i>A</i>)	0.96	0.05	0.43	
Cropland coverage, <i>P_{crop}</i> (% of <i>A</i>)	3.5	46	37	
Water yield (<i>Q</i> , m yr ⁻¹) mean (CV)	0.31 (0.31)	0.26 (0.43)	0.26 (0.33)	
Flow-weighted mean annual concentration, <i>C</i> (mg l ⁻¹), mean (CV)				
	TN	0.64 (0.041)	3.9 (0.10)	2.5 (0.041)
	TP	0.038 (0.075)	0.24 (0.16)	0.20 (0.14)
	TSS	21 (0.16)	77 (0.42)	42 (0.30)
Yield, <i>Y</i> (kg km ⁻² yr ⁻¹), mean (CV)				
	TN	190 (0.26)	990 (0.38)	650 (0.32)
	TP	12 (0.30)	57 (0.48)	53 (0.42)
	TSS	7.5e ³ (0.36)	2.3e ⁴ (0.77)	1.2e ⁴ (0.57)
Retention, <i>R</i> (% of input) based on mean annual export (max)				
	TN	12 (23)	14 (21)	44 (49)
	TP	–	–	35 (45)
	TSS	–	–	38 (48)

^a *FOR* = forested catchments, *AG_{small}* = small agricultural catchments <1000 km², *AG_{large}* = large agricultural catchments >1000 km².

were positively correlated ($p < 0.001$; for TN sites, $r^2 = 0.41$; TP $r^2 = 0.36$; TSS $r^2 = 0.34$). For a given constituent form, significant correlations between *A* and *P_{water}* were lacking within *FOR* and *AG_{small}* catchment classes, but were weakly positively correlated in one catchment class (*AG_{large}*, $p = 0.025$, $r^2 = 0.17$).

Landscape differences in water yield

The period of record (1986–2006) incorporated both high and low discharge years. Across sites, mean annual water yield (*Q_{mean}*) ranged from 0.17 to 0.47 m yr⁻¹, and was 0.20–0.30 m yr⁻¹ at most sites. Catchment class averages for *Q_{mean}* were similar (0.31 m yr⁻¹ in *FOR*, 0.26 m yr⁻¹ in *AG_{small}*, and 0.26 m yr⁻¹ in *AG_{large}*) (Figure 4, Table II). However, forested catchments on average showed 20% higher *Q_{mean}* than agricultural catchments ($FOR > AG_{small}$, $p = 0.005$; $FOR > AG_{large}$, $p = 0.004$) and this was considered for our interpretations of mass export. There was no significant difference in *Q_{mean}* between *AG_{small}* and *AG_{large}* catchments. Interannual variability in water yield (CV_Q) ranged from 0.11 to 0.31 in *FOR* catchments, 0.13 to 0.59 in *AG_{small}* catchments, and 0.16 to 0.60 in *AG_{large}* catchments (Figure 5). *AG_{small}* catchments had, on average, 60% higher water yield variability (CV_Q) than *FOR* catchments ($CV_{Q,AG_{small}}:CV_{Q,FOR} = 1.6$, $p = 0.014$), while *AG_{large}* catchments had intermediate water yield variability ($CV_{Q,AG_{large}}:CV_{Q,FOR} = 1.3$, $p = 0.083$). CV_Q was not significantly different between *AG_{large}* and *AG_{small}* catchments ($CV_{Q,AG_{large}}:CV_{Q,AG_{small}} = 0.82$).

Landscape differences in mass export

Mean yield and concentration were generally higher in agricultural compared to forested catchments (Table III, Figure 4), particularly in smaller catchments with intense agriculture. For instance, *Y_{mean}* was higher in *AG_{small}* compared to *FOR* catchments for all constituents ($p < 0.015$, Fig. 4), and the difference was largest for TN (mean $Y_{AG_{small}}:Y_{FOR} = 5.24$), intermediate for TP (mean $Y_{AG_{small}}:Y_{FOR} = 4.71$), and smallest for TSS (mean $Y_{AG_{small}}:Y_{FOR} = 3.08$). Differences in *Y_{mean}* between *AG_{large}* and *FOR* catchments were smaller but still significant for TN (mean $Y_{AG_{large}}:Y_{FOR} = 3.31$, $p < 0.001$) and TP (mean $Y_{AG_{large}}:Y_{FOR} = 4.34$, $p < 0.001$), although not significant for TSS (mean $Y_{AG_{large}}:Y_{FOR} = 1.55$). The higher export of agricultural compared to forested catchments was not simply explained by differences in water yield, as agricultural catchments had 10–15% lower water yield on average (mean $Q_{AG_{small}}:Q_{FOR} = 0.85$, $p = 0.010$; mean $Q_{AG_{large}}:Q_{FOR} = 0.89$, $p = 0.034$). For TN only, mean yield was 35% lower in large agricultural (*AG_{large}*) compared to small agricultural (*AG_{small}*) catchments, indicating a difference associated with catchment size. Significant long-term increases or decreases in mass yield and flow-weighted mean annual concentration were lacking at most sites over the period of record (Appendix Table A1). Paired comparisons involving flow-weighted concentration (*C_{mean}*) were similar to those involving *Y_{mean}*, as both measures were higher in agricultural catchments compared to forested catchments.

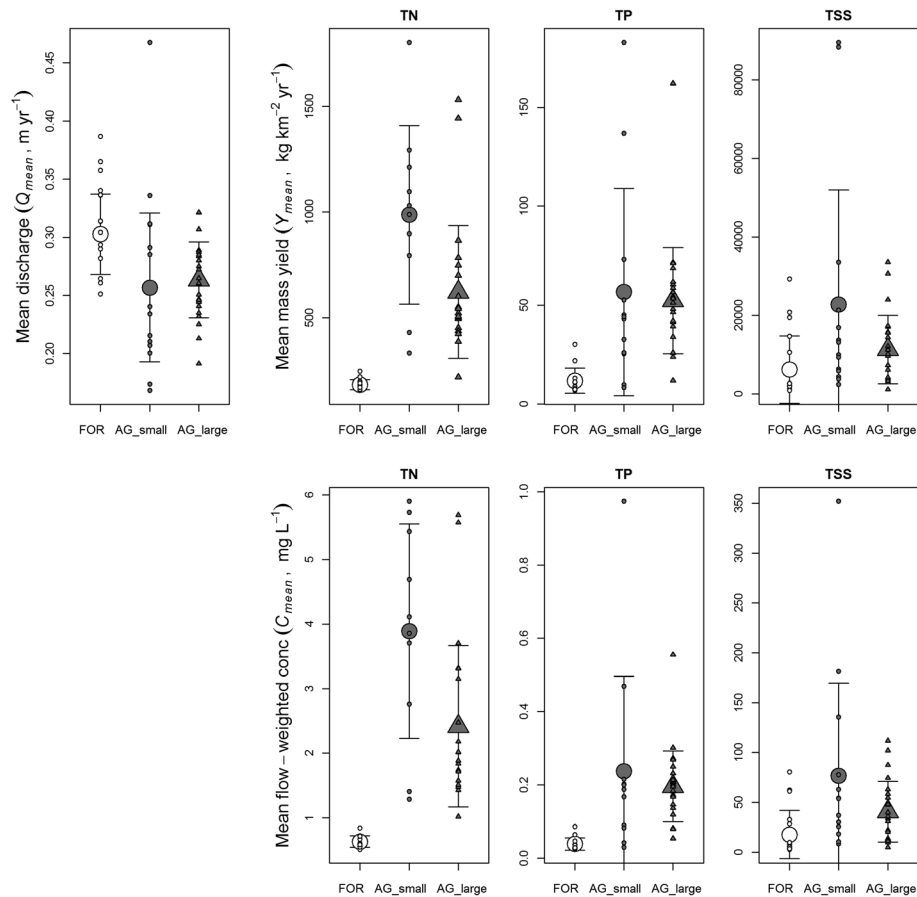


Figure 4. Mean annual water yield, mass yield, and flow-weighted mean annual concentration for total nitrogen (TN), total phosphorus (TP), and total suspended sediment (TSS) at long-term river sampling sites. Larger symbols are group means (± 1 s.d.), and smaller symbols are underlying data from individual stream sites. Key: white circles = forested catchments (*FOR*), gray circles = small (<1000 km²) agricultural catchments (*AG_{small}*), gray triangles = large (>1000 km²) agricultural catchments (*AG_{large}*)

Interannual variability (CV) in mass export varied among catchment classes and was not merely a linear function of water yield variability. For instance, the ratio of mass variability to water variability ($CV_Y:CV_Q$) ranged widely for TSS (0.95–5.49) and TP (0.74–3.86), although TN export more closely followed water variability (0.55–1.67). Mass variability usually exceeded water variability ($CV_Y > CV_Q$) at 98% and 91% of TSS and TP sites, respectively) although 28% of TN sites showed $CV_Y < CV_Q$. For all constituents, CV_Y was higher in *AG_{small}* compared to *FOR* catchments ($p < 0.010$), and the difference was largest for TSS (mean $CV_{Y,AG_small}:CV_{Y,FOR} = 2.16$), intermediate for TP (mean $CV_{Y,AG_small}:CV_{Y,FOR} = 1.64$), and smallest for TN (mean $CV_{Y,AG_small}:CV_{Y,FOR} = 1.49$). Relative differences in concentration variability among catchments were usually consistent with relative differences in yield variability.

Lake and reservoir effects on export magnitude

There was substantially lower export of TN, TP, and TSS in the presence of lakes and reservoirs, particularly

during high loading years. This was represented by significant negative relationships between yield and P_{water} within catchment classes, suggesting lake and reservoir nutrient and sediment retention (Table IV). For instance, in *AG_{large}* catchments, maximum annual TP yield decreased by approximately half as P_{water} increased from 0.02 to 2% (Figure 6). For TSS, there was a similar negative relationship between Y_{max} and $\log_{10} P_{water}$ ($p = 0.030$). For TN export, effects of lakes and reservoirs within an individual catchment class were restricted to *FOR* catchments (Y_{max} , $p = 0.008$; Y_{mean} , $p = 0.098$), although agricultural catchments in aggregate (*AG_{small}* + *AG_{large}*) showed declining TN yield with P_{water} (Y_{max} , $p = 0.009$; Y_{mean} , $p = 0.019$). For TN in *AG_{large}* catchments, the relationship between Y_{max} and P_{water} was not significant, but there was a relationship with P_{res} ($p = 0.024$, $r^2 = 0.43$, slope = -970 ± 350). In terms of r^2 and slope (b_1) values reported in Table IV, effects of lakes and reservoirs on river export were more strongly represented by Y_{max} than Y_{mean} . This suggests the importance of lentic processes during high loading years.

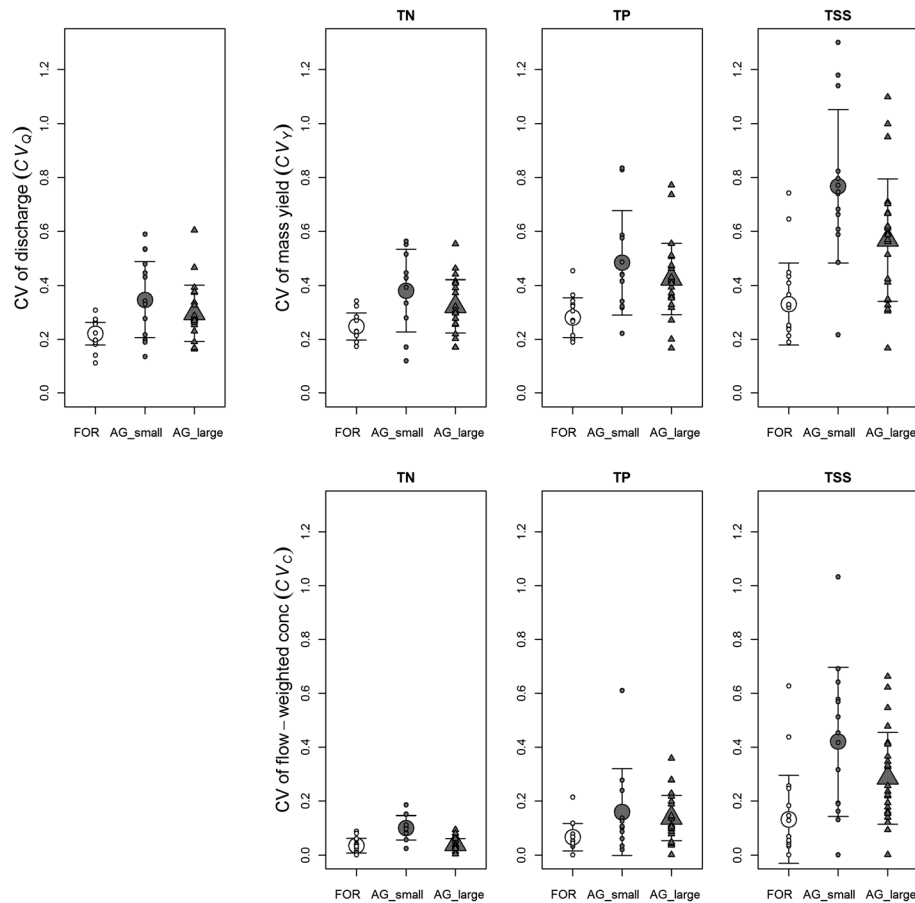


Figure 5. Interannual variability (CV) of water yield, mass yield, and flow-weighted mean annual concentration of total nitrogen (TN), total phosphorus (TP), and total suspended sediment (TSS) at long-term river sampling sites. Larger symbols are group means (± 1 s.d.), and smaller symbols are underlying data from individual stream sites. Key: white circles = forested catchments (*FOR*), gray circles = small ($< 1000 \text{ km}^2$) agricultural catchments (*AG_{small}*), gray triangles = large ($> 1000 \text{ km}^2$) agricultural catchments (*AG_{large}*)

Alternate hypotheses to lentic retention were also considered. Within catchment classes, there were no significant relationships involving yield magnitude and $\log_{10} A$. However, there was evidence of a possible role of wetlands for TP and TSS in years of high loading (negative relationship between Y_{max} and $\log_{10} P_{wetland}$ for TP in *AG_{large}* catchments ($p = 0.047$, $r^2 = 0.14$) and TSS in *AG_{small}* catchments ($p = 0.036$, $r^2 = 0.26$)). It should nonetheless be recognized that there was also a positive relationship between P_{water} and $P_{wetland}$ for *AG_{large}* catchments ($p < 0.001$, $r^2 = 0.45$). No significant relationships involving minimum yield (Y_{min}) and lentic water were found.

Retention as a percentage of mass input (R), calculated based on relationships between mean annual export (Y_{mean}) and P_{water} reported in Table IV, indicated substantial retention in *AG_{large}* catchments for TN (44%), TP (45%), and TSS (38%). *FOR* and *AG_{small}* catchments also showed moderate TN retention (12% and 14%, respectively). TN input (Y_{in}) used to calculate R was $1150 \text{ kg km}^{-2} \text{ yr}^{-1}$ in *AG_{small}* and *AG_{large}* catchments and

$210 \text{ kg km}^{-2} \text{ yr}^{-1}$ in *FOR* catchments. For *AG_{large}* catchments, Y_{in} was $81 \text{ kg km}^{-2} \text{ yr}^{-1}$ for TP and $19000 \text{ kg km}^{-2} \text{ yr}^{-1}$ for TSS. When based on relationships between maximum annual export (Y_{max}) and P_{water} , retention was higher, especially for TN in *FOR* catchments (23%), TN in *AG_{small}* catchments (21%), and TP in *AG_{large}* catchments (45%, Table II).

Lake and reservoir effects on interannual variability in export

There was evidence that lakes and reservoirs reduce interannual variability in TP and TSS export, and to a lesser degree, TN export. This is shown in Figure 7, which relates mass variability (CV_Y) to water variability (CV_Q), and indicates negative relationships between $CV_Y - CV_Q$ and $\log_{10} P_{water}$. These included: reduced TSS variability in *AG_{large}* catchments ($p = 0.002$, $r^2 = 0.35$); reduced TP variability in *AG_{large}* catchments ($p = 0.002$, $r^2 = 0.35$); reduced TP variability in *FOR* catchments (marginally significant, $p = 0.096$, $r^2 = 0.20$); reduced TN variability in *FOR* catchments ($p = 0.035$, $r^2 = 0.34$);

Table III. Paired differences in river export between catchment classes (expressed as ratios). Only comparisons with $p \leq 0.10$ are shown

Measure	Abbrev.	Form	$AG_{small}:FOR$	$AG_{large}:FOR$	$AG_{small}:AG_{large}$
Water yield mean (m yr^{-1})	Q_{mean}	water	0.83, $p=0.005$	0.83, $p=0.004$	–
Water yield variability (CV)	CV_Q	water	1.6, $p=0.014$	–	–
Mean mass yield ($\text{kg km}^{-2} \text{yr}^{-1}$)	Y_{mean}	TN	5.2, $p < < 0.001$	3.4, $p < 0.001$	–
		TP	4.7, $p=0.004$	4.4, $p < < 0.001$	–
		TSS	3.0, $p=0.034$	1.6, $p=0.080$	–
Mean concentration (mg l^{-1})	C_{mean}	TN	6.1, $p < < 0.001$	3.9, $p < 0.001$	–
		TP	6.1, $p=0.001$	5.0, $p < < 0.001$	–
		TSS	3.6, $p=0.008$	1.9, $p=0.026$	–
Mass yield variability (CV)	CV_Y	TN	1.5, $p=0.082$	–	–
		TP	1.6, $p=0.009$	1.4, $p=0.018$	–
		TSS	2.2, $p < 0.001$	1.6, $p=0.039$	–
Concentration variability (CV)	CVC	TN	2.5, 0.010	–	2.5, $p=0.002$
		TP	–	1.8, $p=0.092$	–
		TSS	2.7, $p=0.005$	1.8, $p=0.053$	–

Table IV. Regression statistics that suggest reductions in mass export, or reductions in export variability, by lentic ecosystems. All regressions are of the form $y_i = b_j \log_{10} P_{water} + b_0$, (only $p \leq 0.10$ shown, and these correspond to lines plotted in Figures 6 and 7). Dependent variables are mean yield, maximum yield, and $CV_Y - CV_Q$ (a measure of yield variability relative to discharge variability). Intercepts (b_0) are significant at $\alpha=0.01$ except for one instance (non-significant b_0 for TN $CV_Y - CV_Q$ in $AG_{small} + AG_{large}$). S.E. = standard error

Dependent variable (y)	Constituent form	Catchment class	Independent variable ($\log_{10} x$)	$b_1 \pm 1 \text{ s.e.}$	p	r^2
Y_{mean}	TN	FOR	P_{water}	-29 ± 16	0.098	0.19
Y_{mean}	TN	$AG_{small} + AG_{large}$	$P_{water}^{L,R}$	-175 ± 70	0.019	0.16
Y_{mean}	TP	AG_{large}	P_{water}^L	-23 ± 9.6	0.024	0.18
Y_{mean}	TSS	AG_{large}	P_{water}^L	$-6.1e3 \pm 2.8e3$	0.042	0.14
Y_{max}	TN	FOR	$P_{water}^{L,R}$	-93 ± 27	0.008	0.52
Y_{max}	TN	$AG_{small} + AG_{large}$	$P_{water}^{L,R}$	-430 ± 150	0.009	0.20
Y_{max}	TP	AG_{large}	$P_{water}^{L,R}$	-82 ± 24	0.003	0.33
Y_{max}	TSS	AG_{large}	P_{water}^L	$-2.9e4 \pm 1.2e4$	0.030	0.17
$CV_Y - CV_Q$	TN	FOR	P_{water}^L	-0.048 ± 0.019	0.035	0.34
$CV_Y - CV_Q$	TN	$AG_{small} + AG_{large}$	$P_{water}^{L,R}$	-0.028 ± 0.012	0.027	0.14
$CV_Y - CV_Q$	TP	AG_{large}	$P_{water}^{L,R}$	-0.11 ± 0.032	0.002	0.35
$CV_Y - CV_Q$	TP	FOR	P_{water}^L	-0.073 ± 0.039	0.096	0.20
$CV_Y - CV_Q$	TSS	AG_{large}	$P_{water}^{L,R}$	-0.20 ± 0.055	0.002	0.35

^L Negative relationship between y and P_{lake} also significant ($p \leq 0.05$).

^R Negative relationship between y and P_{res} also significant ($p \leq 0.05$).

reduced TN variability for AG_{small} and AG_{large} catchments combined ($p=0.027$, $r^2=0.14$). The presence of significant negative relationships between $CV_Y - CV_Q$ and $\log_{10} P_{water}$ within catchment classes indicates these patterns cannot be merely explained from differences in cropland coverage or catchment size. For AG_{small} catchments, $CV_Y - CV_Q$ was not related to lentic water variables, which is likely due to the higher spread of $CV_Y - CV_Q$ in this catchment class, as well as the scarcity of lakes and reservoirs in some catchments. Within catchment classes, there were no significant relationships involving $CV_Y - CV_Q$ and catchment area, except for TSS for AG_{large} catchments ($p=0.021$, $r^2=0.19$). Interannual variability in concentration (CV_C) was highly positively

correlated with $CV_Y - CV_Q$ (TN, $r^2=0.27$, $p < 0.001$; TP, $r^2=0.81$, $p < 0.001$; TSS, $r^2=0.92$, $p < 0.001$), but $CV_Y - CV_Q$ included a few negative values, and so provided a larger gradient for analyses than CV_C . Data for individual sites are in the Appendix.

DISCUSSION

Streams and rivers route matter through landscapes into downstream ecosystems, and often show substantial interannual variability in the mass delivered, even between consecutive years. Compared to long-term changes in mass export caused by changes in land use

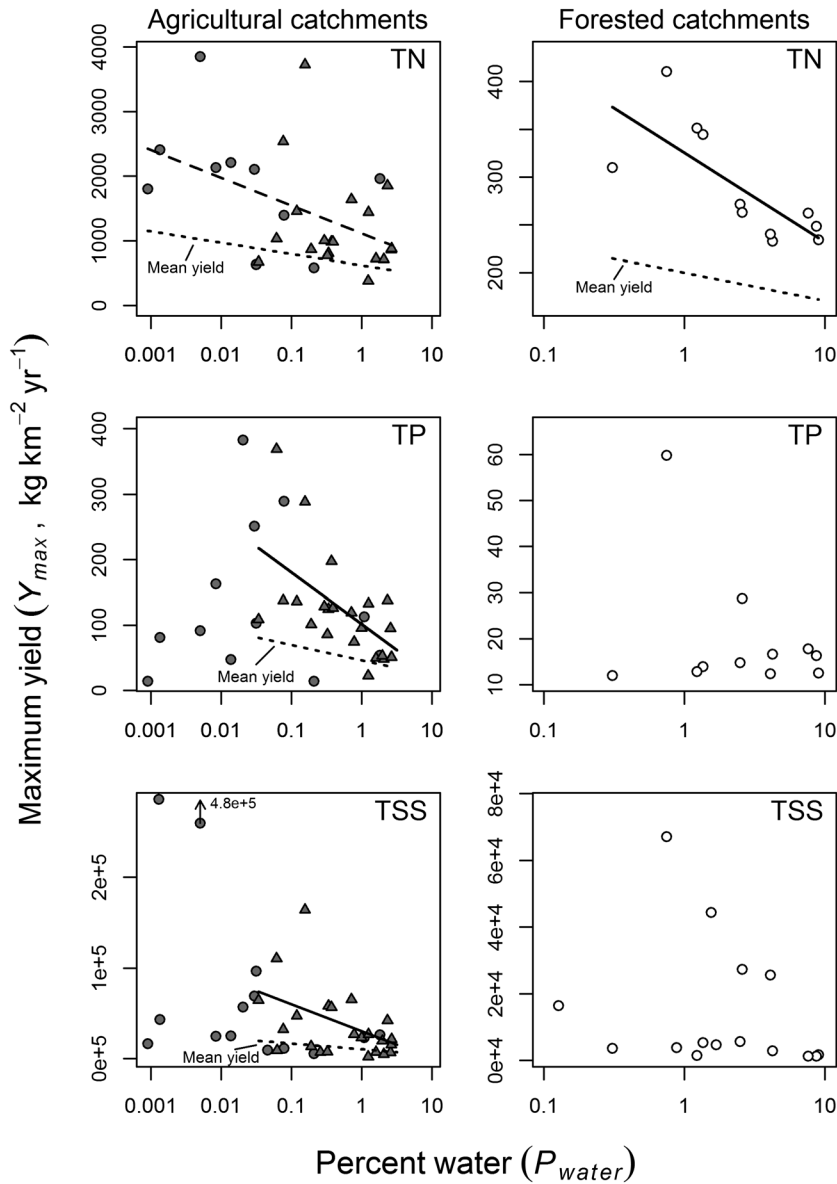


Figure 6. Maximum annual mass yields for each river site in relation to the percentage of lentic water in the catchment (P_{water}). Significant negative relationships, including both maximum yields (data plotted) and mean yields (data not plotted), are shown in Table IV and suggest mass retention by lakes and reservoirs. Key: white circles=forested catchments (FOR), gray circles=small ($<1000 \text{ km}^2$) agricultural catchments (AG_{small}), gray triangles=large ($>1000 \text{ km}^2$) agricultural catchments (AG_{large}). Lines: solid=significant trend within catchment class; dashed=significant trend for $AG_{small} + AG_{large}$ catchments; dotted=significant trend for mean yield (Y_{mean})

or climate, these year-to-year differences are more easily quantified, certain to occur, and have immediate relevance to current water resources and biota. Further, while variability in river mass export is driven largely by variability in total precipitation (Alexander *et al.*, 1996; Goolsby and Battaglin, 2001), export responses to precipitation are not uniform across landscapes (Martin *et al.*, 2004). There is a need to understand why this is so. Here, in two contrasting landscapes (agricultural, forested), we examined long-term (20 years) records to show effects of lakes and reservoirs on river export. Our results demonstrate that lentic ecosystems have a dynamic role within river

networks that influences long-term export of nutrients and sediment. Specifically, we provide evidence that lakes and reservoirs not only reduce the magnitude of river mass export for multiple constituents, but also stabilize interannual export variability. Differences in export of river nitrogen, phosphorus, and sediment undoubtedly reflect the different pathways affecting the movement of these materials through terrestrial and lentic ecosystems.

Effects of reservoirs and lakes on river export appeared to be more strongly represented by the maximum annual yield and the yield CV compared to the mean annual yield. This suggests lentic ecosystems reduce peak loads

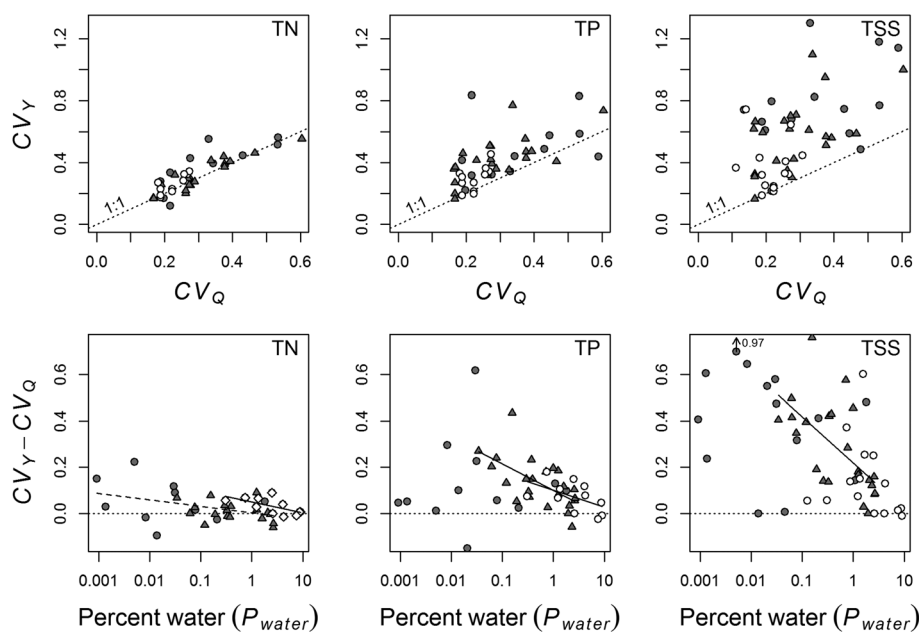


Figure 7. Interannual variability in mass yield (CV_Y) compared to interannual variability in water yield (CV_Q) and the percentage of lentic water in catchment (P_{water}). Dotted line in top panel is 1:1 line. Negative relationships in residual plots ($CV_Y - CV_Q$ as a function of P_{water}) suggest stabilization of mass yield variability by lentic water bodies. One point in lower right panel falls outside of plotted axes (TSS, $CV_Y - CV_Q = 0.97$). Key: white circles = forested catchments (FOR), gray circles = small (<1000 km²) agricultural catchments (AG_{small}), gray triangles = large (>1000 km²) agricultural catchments (AG_{large}). Lines: solid = significant trend for $CV_Y - CV_Q$ within catchment class; dashed = significant trend for $AG_{small} + AG_{large}$ catchments

during high loading years. Further, our results emphasized a similar qualitative role of lentic ecosystems in agricultural and forested landscapes over the long-term. This role is summarized in Figure 8 for TN, TP, and TSS, which shows two main results that we expand upon below. First, the magnitude of mass export (mean or max yield) was lower in lentic catchments (those containing a higher percentage of lake or reservoir water) than lotic catchments (Figure 6), suggesting nutrient burial, lentic denitrification, and sedimentation. Second, for lotic catchments, interannual variability of export (as represented by the CV) was highest for TSS, intermediate for TP, and lowest for TN in lotic catchments, while for lentic catchments there was reduced interannual variability in export for all river constituents.

Retention in lakes and reservoirs

There were multiple lines of evidence that lakes and reservoirs reduce the magnitude of river nutrient and sediment export. First, for both agricultural and forested catchments, there was lower maximum annual as well as mean annual TN export in the presence of lakes and reservoirs. Second, for TP and TSS export from large agricultural (AG_{large}) catchments, there were similar negative relationships with lentic water (on average one third of mass inputs retained, by our approximation). We argue these results are best explained by net retention/loss in lakes and reservoirs, which is supported by

previous aquatic N studies (Wollheim *et al.*, 2008; Harrison *et al.*, 2009; Vanni *et al.*, 2010) and presumably caused by sedimentation, nutrient burial, or in the case of N, denitrification (Molot and Dillon, 1993; David *et al.*, 2006). Certainly, wetland and stream denitrification can also be important in agricultural catchments, but for our study, it appears that most denitrification (quantified as net N reduction, as N removal can be partly offset by N-fixation) occurred in lakes and reservoirs. For instance, within catchment classes, there were no significant negative relationships involving TN yield and $\log_{10} P_{wetland}$ (potentially indicative of wetland denitrification), or TN yield and catchment area (potentially indicative of cumulative stream or river denitrification). We suggest the relationship between TN retention and catchment size demonstrated across catchments (lower mean TN yield in AG_{large} compared to AG_{small} catchments) is most likely caused by cumulative lentic retention along the river network, or alternatively, a combination of lentic retention and stream retention.

The importance of lentic water bodies within agricultural catchments is particularly evident in terms of total mass, because these systems generally have much higher mean annual TN, TP, and TSS loading compared to those in forested catchments. But it is also possible that the contributions of lakes *versus* reservoirs to total lentic retention could vary among landscapes. For instance, AG_{large} catchments showed a fairly balanced representation

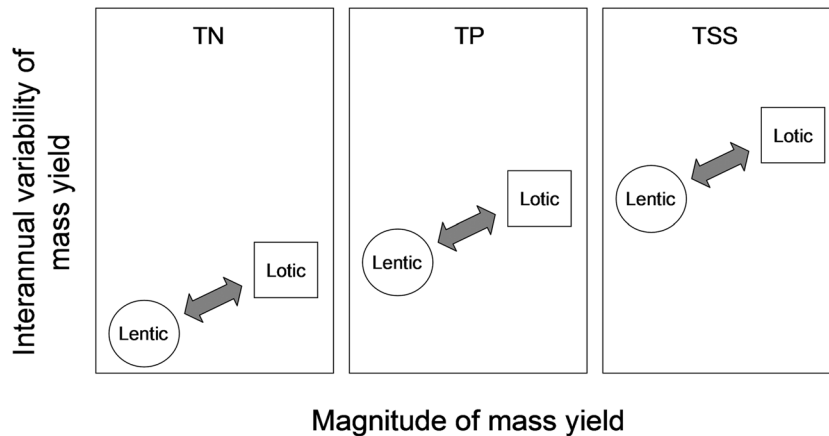


Figure 8. Summary of mass export from lentic catchments (lakes/reservoirs present, circles) compared to lotic catchments (lakes/reservoirs absent, squares). The relative variability of different constituents (positions along Y axis) is inferred from our results

for lakes and reservoirs within the river network (similar P_{res} and P_{lake}), while lentic water in forested catchments was more dominated by P_{lake} . This could mean that TN retention in forested catchments was primarily associated with natural lake processes, whereas agricultural catchments contain a mix of artificial reservoir and natural lake processes. However, it is not possible to directly partition effects of reservoirs from lakes in our analysis because relationships involving river export and P_{water} were often supplemented by similar negative relationships involving both P_{lake} and P_{res} (see Table IV). Further research is needed to partition the effects of different types of lentic ecosystems on river export, and could relate to differences in the configuration (positioning) of these ecosystems within river networks.

It could be argued that higher TN yields for AG_{small} compared to AG_{large} catchments are attributable to a systematic difference in TN loading, not effects of TN retention. However, this alternative explanation does not appear sufficient for three reasons. First, if the observed difference in TN yield was attributable to differences in *nonpoint TN sources*, this might be accompanied by corresponding differences in cropland coverage. However, cropland coverage was similar for AG_{large} and AG_{small} catchments, both in terms of mean P_{crop} ($AG_{small}=46\%$, $AG_{large}=37\%$, not significantly different) and range of P_{crop} ($AG_{small}=16\text{--}68\%$, $AG_{large}=15\text{--}61\%$). Second, if the difference in yield was attributable to differences in *TN point sources*, this might be accompanied by corresponding differences in urban coverage. Yet mean urban coverage was similar (mean $P_{urban}=5.9\%$ in AG_{large} catchments compared to mean $P_{urban}=6.2\%$ in AG_{small} catchments), and low overall (P_{urban} range= $2.1\text{--}10\%$). Third, if the difference in yield was attributable to differences in *groundwater TN sources*, this might be accompanied by corresponding differences in water yield (for a given groundwater TN) because catchments with higher water yield often have larger inputs of groundwater. However,

mean annual water yield was not significantly different between AG_{large} and AG_{small} catchments. Therefore, we argue that the difference in TN yield between AG_{large} and AG_{small} catchments is not attributable to a systematic difference in TN loading, and rather is best explained by TN retention.

Although we have emphasized nutrient and sediment retention in lakes and reservoirs, it is important to recognize that significant lentic retention was not always detected in our analysis. For instance, there were no significant declines in river TP or TSS export associated with the amount of lentic water in *FOR* and AG_{small} catchments. These null results are probably best interpreted as low TP and TSS sedimentation in lentic ecosystems relative to inputs, not negligible gross sedimentation, but further discussion is warranted. Limnological research has emphasized P sedimentation in lakes as a mechanism of nutrient removal (Wodka *et al.*, 1985; Schindler *et al.*, 1993; Essington and Carpenter, 2000; Vanni *et al.*, 2010). We offer three possibilities to explain the absence of substantial lentic P sinks in *FOR* and AG_{small} catchments. First, it is possible that modest wastewater/point P sources (Carey and Migliaccio, 2009), or nonpoint P sources not represented by the P_{crop} gradient, offset lake and reservoir P sinks, masking their gross effect. We have provided some protection against this possibility by excluding sites near wastewater treatment outflows and urban areas, but recognize it cannot be completely eliminated. Second, recycling of large internal/legacy P pools in reservoirs (Powers *et al.*, 2013) or rivers (Jarvie *et al.*, 2012) may provide P sources that counter-balance gross annual P retention, especially in low flow years when recycled P and desorbed P from the benthos may contribute a higher fraction of overall river P. Similarly, our findings of significantly lower maximum annual TP yield in the presence of lentic water, but no relationship between lentic water and minimum

annual TP yield (Figure 6), may be indications that P retained in high loading years becomes a P source to rivers in later years (a transport time lag; Hamilton, 2012). Third, storage sites for P in shallower lakes and reservoirs may be declining with ongoing sedimentation or P accumulation, shifting historical P sinks toward P balance. The two previous explanations may co-occur and are potentially major concerns for water resources.

Stabilization of river export variability by lakes and reservoirs

In the presence of lakes and reservoirs, there was lower variability of TP and TSS export, and to a lesser degree, lower variability of TN export. Strong evidence that lakes and reservoirs reduce P and sediment variability is provided by $CV_Y - CV_Q$ (the difference between mass variability and water variability), which decreases along a gradient of catchment water body coverage (P_{water}) as shown in Figure 7. This further indicates the lower interannual variability in yields for AG_{large} compared to AG_{small} catchments in Figure 5 cannot be explained entirely by variability in water yield. Nor can decreasing $CV_Y - CV_Q$ with the amount of lentic water be explained by differences among regions or catchment sizes, because the negative relationship was upheld within the catchment classes. Rather, these patterns suggest that processes in lentic ecosystems are reducing river TP and TSS variability. A similar stabilizing effect of lakes has been observed over short time frames for stream dissolved organic matter (Goodman *et al.*, 2011) and nitrogen (Wurtsbaugh *et al.*, 2005). Our finding of reduced variability of TN and TP in the presence of lakes and reservoirs is likely linked to substantial retention in high loading years, as represented by the analysis of maximum annual yields. However, N or P retained in a given year can be recycled and released to streams and rivers in future years, or simply take longer to pass through the system when water residence time is >1 year (as is the case for larger lakes and reservoirs). For these reasons, retention at an annual interval cannot always be viewed as a long-term sink.

The lower variability of TP compared to TSS provides new evidence that river P export is buffered over the long term. Presumably, this involves a combination of physico-chemical pathways (sorption/desorption) in agricultural soils (Sharpley *et al.*, 1981) as well as in aquatic ecosystems (Haggard *et al.*, 1999; Reddy *et al.*, 1999), including biological P pathways such as recycling of P in lakes (Carpenter *et al.*, 1992) or streams (Jarvie *et al.*, 2012). The movement of legacy P from lentic ecosystems into rivers could be a particularly important P source in years of lower flow and loading, although minimum annual yields did not show significantly higher TP export

in the presence of lakes or reservoirs. Meanwhile, the ability of lakes and reservoirs to substantially modify river TN variability was limited by smaller interannual deviations in TN yield relative to TP and TSS. The long-term stability of TN loading is likely a reflection of steady sources of groundwater N and leakiness of N overall, which prevents its substantial accumulation in soils. It is also possible that higher aquatic denitrification in low water years, perhaps in response to increased sediment–water contact (Alexander *et al.*, 2000) or higher water temperature, could produce disproportionately low minima for TN in the presence of lakes/reservoirs.

Terrestrial landscape effects on stream nutrient export

Agricultural catchments not only had significantly higher mean TN and TP yields, but also higher yield variability. Overall, interannual variability in TP yield was larger than TN yield, which likely reflects different patterns of accumulation and mobilization for these elements within landscapes. For example, transient P accumulation in agricultural soils can be followed by disproportionate mobilization during high precipitation years that promote erosion of hillslopes and stream banks (Sharpley *et al.*, 2001). In contrast, steady sources of soil and dissolved inorganic N can represent a large fraction of river TN (Kennedy *et al.*, 2012), in particular when groundwater N discharge is large. It is also important to note that forested catchments had glaciated sandy/loamy forest soils, whereas agricultural catchments had primarily silty/loamy prairie soils. These differences in lithology, which are associated with latitude, do not allow for a perfect comparison of cropland effects in our analysis.

Linkages between river export and catchment size

For TN, yield variability was lower in larger agricultural catchments ($AG_{large} < AG_{small}$, see Table III), and we argue that dynamic processes in lakes and reservoirs contribute to this difference. However, export from larger catchments is also stabilized by other factors. For example, point sources from wastewater are often released within larger river valleys containing higher urban development, and this can drown out variability of other sources. Also, large catchments integrate many distant and independent mass sources to rivers, so tributary deviations may sometimes occur asynchronously, or in opposite directions, thus limiting aggregate variability. These concerns necessitated our comparisons among catchments with similar area in order to understand effects of lakes and reservoirs on river export. Thus, catchment size may contribute to biogeochemical stationarity (chemostasis) in rivers (Basu *et al.*, 2010; Thompson *et al.*, 2011). However, because effects of lakes and reservoirs on river export may also accumulate

along the river network, while larger reservoirs are often positioned in larger river valleys, apparent effects of catchment size on river export may sometimes be better understood as effects of lentic ecosystems.

CONCLUSION

In this work, we have shown that lakes and reservoirs within river networks not only reduce the magnitude of annual river mass export, but also reduce interannual variability in export. Thus, our results demonstrate that lentic ecosystems have an important and dynamic role within river networks over the long-term. Overall, TSS export (concentration and yield) had the highest variability, followed by TP and TN, but there was convergence toward common interannual variability in catchments possessing lakes and reservoirs. The combination of retention and stabilization of variability by lakes and reservoirs has consequences for river nutrient stoichiometry. In agricultural catchments that lack lakes and reservoirs, we speculate that N:P ratios may decrease in high precipitation years caused by disproportionately high P transport relative to N, perhaps especially when accumulated soil P is released following years of below-average precipitation. Nonetheless, it is important to recognize that N retention in agricultural catchments was usually small relative to TN loading, as was P retention relative to TP loading, except when coverage by lakes and reservoirs was especially high (Figure 6). Long-term export through rivers depends on interacting terrestrial, aquatic, and meteorological factors in which the presence of lakes and reservoirs can reduce the magnitude of export, stabilize interannual variability in export, as well as introduce export time lags.

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APPENDIX A. ESTIMATION OF ANNUAL LOADS

Annual TN, TP, and TSS loads for each monitored stream/river site were computed with the rating curve/regression procedure in the Fluxmaster computer program (Schwarz *et al.*, 2006). The effectiveness of this approach, which uses statistical relationships between daily discharge and daily concentration to estimate annual loads from a continuous record of daily discharge, is described in detail in Saad *et al.* (2011). All sites in the analysis met the screening criteria for annual load estimation presented in Saad *et al.* (2011).

Within Fluxmaster, we used a water-quality model (Equation 1) that relates the logarithm of observed concentration at time t (c_t) to the logarithm of discharge (q_t), a decimal time term to represent trend (T_t), sine and cosine functions of decimal time to account for seasonal variation, and a model residual (e_t),

$$c_t = b_0 + b_q q_t + b_T T_t + b_s \sin(2\pi T_t) + b_c \cos(2\pi T_t) + e_t \quad (1)$$

where b_0 , b_q , b_T , b_s , and b_c are fixed coefficients for each site that are estimated by the ordinary least squares method, or if some of the c_t measurements are censored, by the adjusted maximum likelihood method, and e_t is assumed to be independent and normally distributed with mean 0 and variance σ_e^2 . Daily loads (l_t , kg) for each site were then estimated from $c_t \times q_t$, and summed for each water year to estimate annual loads (L_t , kg).

APPENDIX B. LONG-TERM TRENDS AND DETRENDING

For the subset of sites that showed significant long-term linear trends in Y_t , or C_t , annual time series were linearly detrended (to the long-term median) in order to best eliminate effects of management or land-use change. However, most sites lacked significant long-term trends, or had relatively small significant trends. For both Y_t and C_t , large trends (>50% change from initial conditions) were restricted primarily to TSS (four sites had large trends in Y_t , seven sites had large trends in C_t), with only one site for TN and one site for TP having changes >50% for either Y_t and C_t (Table A1). Overall, for TN, two of three significant trends in Y_t were positive, as were 13 of 17 significant trends in C_t . In contrast, for TP, four of five significant trends in Y_t were negative, as were 13 of 17 significant trends in C_t . For TSS, four of five significant trends in Y_t were positive, as were 11 of 17 significant trends in C_t . In most of these cases, detrending resulted in only a modest reduction (<25%) for CV_Y or CV_C . No site had a long-term linear trend for Q_r . A summary of the data for each site is provided in Table A2.

APPENDIX C. LAND-COVER RELATIONSHIPS

Land-cover variables are often correlated and require consideration when interpreting landscape patterns and effects. Figure A1 shows all paired relationships for land-cover variables considered in the analysis (WDNR, 2009). Land-cover variables were aggregated from NLCD

classifications as follows: P_{crop} = cultivated crops, P_{for} = deciduous, evergreen, or mixed forest, P_{urb} = high, medium, or low intensity development or developed open space, P_{wet} = emergent herbaceous wetland. The strongest correlation (negative) was between P_{crop} and P_{for} ($r^2 = 0.72$), which justifies our classification of low P_{crop} catchments as predominantly forested (FOR). There were also notable positive correlations between P_{lake} and P_{res} ($r^2 = 0.51$), and between P_{urb} and P_{for} ($r^2 = 0.58$). Because the analysis focused primarily on relationships between mass export and P_{lake} or P_{res} within each catchment class (FOR = forested, AG_{small} = small agricultural, AG_{large} = large agricultural), it is especially important to consider within-class paired relationships. With exceptions addressed in the manuscript body, within-class correlations between the variables A , P_{crop} , P_{lake} , P_{res} , and P_{wet} (herbaceous wetland) were lacking, and this is apparent from visual inspection of the scatter for a given symbol in panels of Figure A1. While sites in the analysis were restricted to predominantly rural catchments ($P_{urb} < 10\%$), modest point sources from urban areas may have contributed to mass export of TP, and to a lesser degree TN, from AG_{small} and AG_{large} catchments. This statement is founded upon the biased distribution of urban land in catchments that also had higher cropland (positive correlation between P_{urb} and P_{crop} , $r^2 = 0.36$). Overall, the study region had substantial heterogeneity and a large range for the main variables of interest (A , P_{crop} , P_{water}). Changes in land cover over the period of record, as represented by the National Land Cover Dataset (NLCD 1992 and 2006), were relatively modest except in urban catchments not included in the analysis.

Table A1. Sites with long-term linear trends in river yield (Y_t) and flow-weighted mean annual concentration (C_t). Only sites with long-term trends >50% (positive or negative) from initial conditions are shown. S.E. = standard error

Metric	Form	Site	<i>n</i> (years)	Slope	Slope s.e.	Slope <i>p</i>	Int	Int s.e.	Int <i>p</i>	<i>r</i> ²	% change from initial condition
Y	TN	173208	21	1.1E+01	3.3E+00	0.0035	-2.1E+04	6.6E+03	0.0042	0.34	54
Y	TP	4086500	18	-2.3E+00	4.3E-01	<0.001	4.6E+03	8.5E+02	<0.001	0.62	-76
Y	TS	373325	21	-2.1E+02	9.0E+01	0.028	4.3E+05	1.8E+05	0.027	0.19	-77
Y	TS	4077630	14	-4.7E+02	9.9E+01	<0.001	9.3E+05	2.0E+05	<0.001	0.62	-99
Y	TS	4027500	21	-8.3E+02	3.5E+02	0.031	1.7E+06	7.1E+05	0.029	0.18	-76
Y	TS	4072050	18	1.2E+03	4.9E+02	0.029	-2.3E+06	9.8E+05	0.030	0.22	354
C	TN	4072050	18	1.6E-01	2.9E-02	<0.001	-3.1E+02	5.7E+01	<0.001	0.64	64
C	TP	4086500	18	-4.9E-03	2.8E-04	<0.001	9.9E+00	5.5E-01	<0.001	0.95	-59
C	TS	103094	20	8.9E-01	1.6E-01	<0.001	-1.8E+03	3.3E+02	<0.001	0.60	139
C	TS	4077630	14	-1.0E+00	1.1E-01	<0.001	2.1E+03	2.2E+02	<0.001	0.87	-87
C	TS	4027500	21	-2.2E+00	7.6E-01	0.0098	4.4E+03	1.5E+03	0.0092	0.27	-73
C	TS	313038	18	-1.5E+00	4.7E-01	0.0055	3.0E+03	9.3E+02	0.0052	0.35	-70
C	TS	373325	21	-6.0E-01	1.2E-01	<0.001	1.2E+03	2.5E+02	<0.001	0.52	-70
C	TS	5426000	21	1.9E+00	6.1E-01	0.0053	-3.8E+03	1.2E+03	0.0060	0.31	76
C	TS	4072050	18	7.5E+00	6.9E-01	<0.001	-1.5E+04	1.4E+03	<0.001	0.87	525

Table A2. Land cover and export variables for individual sites. Values for P_{agr}, P_{water}, P_{res}, and P_{lake} are listed here as the proportion of catchment area.

Class	Site	A	P _{crop}	P _{water}	P _{res}	P _{lake}	Q _{mean}	CV _Q	Y _{mean} (kg km ⁻² yr ⁻¹)				CV _Y				C _{mean} (mg l ⁻¹)			
									TN	TP	TSS	TN	TP	TSS	TN	TP	TSS	TN	TP	TSS
FOR	343033	1.2E+03	3.4E-02	4.2E-02	1.0E-02	3.2E-02	3.1E-01	1.9E-01	1.8E+02	1.1E+01	1.8E+03	1.7E-01	2.7E-01	3.2E-01	5.7E-01	3.5E-02	5.6E+00			
FOR	383001	2.9E+03	1.1E-01	1.2E-02	3.9E-03	8.4E-03	2.6E-01	2.6E-01	2.2E+02	7.5E+00	8.7E+02	2.8E-01	3.2E-01	3.3E-01	8.4E-01	2.8E-02	3.5E+00			
FOR	4025500	3.9E+02	1.5E-03	1.7E-02	1.7E-02	1.0E-05	3.9E-01	1.1E-01		2.5E+03				3.7E-01		6.3E+00				
FOR	4027500	7.0E+02	9.8E-03	1.6E-02	1.5E-02	2.3E-04	3.4E-01	1.4E-01		1.5E+04				7.4E-01		3.3E+01				
FOR	4027595	2.5E+03	1.6E-02	7.5E-03	7.5E-05	7.4E-03	3.4E-01	2.7E-01	2.5E+02	3.0E+01	2.9E+04	3.4E-01	4.5E-01	6.5E-01	8.6E-02	8.0E+01				
FOR	4063700	3.6E+02	1.2E-02	3.1E-03	7.4E-05	3.0E-03	2.5E-01	2.7E-01	1.8E+02	6.9E+00	2.1E+03	3.2E-01	3.4E-01	3.2E-01	2.6E-02	8.3E+00				
FOR	4071000	1.8E+03	7.6E-02	1.4E-02	2.2E-03	1.1E-02	2.6E-01	2.6E-01	1.9E+02	7.3E+00	2.7E+03	3.2E-01	3.6E-01	4.1E-01	2.7E-02	9.9E+00				
FOR	4075050	1.3E+03	3.9E-02	4.1E-02	9.7E-03	3.1E-02	3.1E-01	1.9E-01	1.7E+02	7.9E+00	1.9E+04	2.3E-01	3.1E-01	1.9E-01	2.5E-02	6.2E+01				
FOR	4075365	1.8E+02	6.0E-02	1.3E-03	1.3E-03	1.0E-05	3.6E-01	2.0E-01		1.0E+04				2.5E-01		2.9E+01				
FOR	4077100	2.1E+03	4.1E-02	2.6E-02	5.8E-03	2.0E-02	3.4E-01	1.9E-01	2.0E+02	2.2E+01	2.1E+04	1.9E-01	1.9E-01	1.9E-01	6.4E-02	6.1E+01				
FOR	443001	2.0E+03	1.5E-02	8.7E-02	2.3E-02	6.3E-02	2.9E-01	2.2E-01	1.7E+02	1.1E+01	8.8E+02	2.3E-01	2.7E-01	2.5E-01	3.7E-02	3.1E+00				
FOR	443002	2.8E+03	1.9E-02	7.6E-02	1.8E-02	5.8E-02	2.8E-01	2.2E-01	1.8E+02	1.3E+01	8.3E+02	2.1E-01	2.0E-01	2.4E-01	4.6E-02	2.9E+00				
FOR	443003	1.8E+03	1.5E-02	9.0E-02	2.3E-02	6.7E-02	2.9E-01	2.2E-01	1.6E+02	8.9E+00	1.3E+03	2.3E-01	2.1E-01	2.1E-01	3.0E-02	4.3E+00				
FOR	5333500	4.0E+03	1.1E-02	2.5E-02	7.6E-03	1.7E-02	3.0E-01	1.8E-01	1.6E+02	7.4E+00	2.5E+03	2.7E-01	3.3E-01	4.3E-01	2.4E-02	7.9E+00				
FOR	5393500	2.3E+02	6.8E-02	8.8E-03	8.6E-03	1.7E-04	3.6E-01	3.1E-01		1.9E+03				4.5E-01		5.2E+00				
AG _{small}	133417	1.2E+02	5.0E-01	1.4E-04	7.5E-05	6.3E-05	3.1E-01	2.2E-01	1.8E+03	2.6E+01	1.7E+04	1.2E-01	3.2E-01	2.2E-01	5.9E+00	8.2E-02	5.4E+01			
AG _{small}	313038	3.5E+02	2.3E-01	8.4E-05	3.1E-05	5.3E-05	2.1E-01	5.3E-01	9.9E+02	5.3E+01	6.2E+03	5.1E-01	8.3E-01	1.2E+00	4.7E+00	2.0E-01	1.8E+01			
AG _{small}	373325	5.8E+02	6.7E-01	7.8E-04	2.6E-04	5.2E-04	2.9E-01	4.3E-01	8.0E+02	1.4E+02	3.7E+03	4.5E-01	4.9E-01	7.5E-01	2.8E+00	4.7E-01	1.1E+01			
AG _{small}	4072050	2.4E+02	5.8E-01	1.4E-05	1.0E-05	1.4E-05	1.7E-01	5.3E-01	1.0E+03	3.3E+01	1.4E+04	5.6E-01	5.8E-01	7.7E-01	5.4E+00	1.9E-01	7.8E+01			
AG _{small}	4073468	1.4E+02	6.7E-01	1.1E-02	5.8E-03	5.0E-03	2.4E-01	4.5E-01		4.4E+01	9.2E+03		5.7E-01	5.9E-01	1.7E-01	3.7E+01				
AG _{small}	4077630	3.4E+02	1.6E-01	2.1E-03	4.3E-04	1.6E-03	3.4E-01	2.0E-01	4.3E+02	9.9E+00	2.4E+03	1.7E-01	2.2E-01	6.1E-01	1.3E+00	2.9E-02	8.5E+00			
AG _{small}	4085395	2.6E+02	5.0E-01	4.6E-04	3.0E-05	4.3E-04	1.7E-01	4.8E-01		4.3E+03				4.8E-01		2.6E+01				
AG _{small}	4086500	2.9E+02	4.3E-01	1.8E-02	1.0E-05	1.8E-02	2.9E-01	3.4E-01	1.1E+03	2.5E+01	9.9E+03	3.9E-01	4.4E-01	8.2E-01	3.7E+00	8.9E-02	3.0E+01			
AG _{small}	5401050	2.5E+02	5.3E-01	9.1E-06	1.0E-05	9.1E-06	2.1E-01	2.8E-01	9.0E+02	8.4E+00	5.8E+03	4.3E-01	3.2E-01	6.8E-01	4.1E+00	4.1E-02	2.6E+01			
AG _{small}	5406500	1.2E+02	2.8E-01	3.0E-04	1.0E-05	3.0E-04	3.1E-01	2.2E-01	1.2E+03	7.3E+01	2.1E+04	3.3E-01	8.4E-01	8.0E-01	3.9E+00	2.2E-01	6.3E+01			
AG _{small}	5407500	3.9E+02	3.9E-01	3.1E-04	2.7E-04	4.4E-05	2.3E-01	1.9E-01	3.3E+02	4.5E+01	3.4E+04	2.8E-01	4.1E-01	6.6E-01	1.4E+00	1.9E-01	1.4E+02			
AG _{small}	5413500	7.0E+02	5.6E-01	5.1E-05	1.5E-05	3.5E-05	2.2E-01	3.3E-01	1.3E+03	4.3E+01	8.8E+04	5.5E-01	3.4E-01	1.3E+00	5.7E+00	2.0E-01	3.5E+02			
AG _{small}	5423510	2.9E+02	6.5E-01	2.0E-04	1.0E-05	2.0E-04	2.0E-01	5.9E-01		1.8E+02	1.3E+04		4.4E-01	1.1E+00	9.7E-01	5.4E+01				
AG _{small}	5436010	1.7E+02	3.6E-01	1.3E-05	1.3E-05	1.0E-05	4.7E-01	1.3E-01		9.0E+04				7.4E-01		1.8E+02				
AG _{large}	123094	1.8E+03	5.0E-01	1.9E-03	6.5E-04	1.3E-03	2.7E-01	3.8E-01	5.1E+02	5.1E+01	6.1E+03	3.7E-01	4.3E-01	5.7E-01	1.9E+00	1.8E-01	2.1E+01			
AG _{large}	123017	1.8E+03	3.2E-01	3.4E-04	2.0E-04	1.4E-04	2.6E-01	1.9E-01	3.9E+02	4.6E+01	2.4E+04	2.6E-01	4.6E-01	6.0E-01	1.5E+00	1.7E-01	8.7E+01			
AG _{large}	173051	4.9E+03	2.7E-01	2.0E-02	9.4E-03	1.0E-02	2.9E-01	1.7E-01		3.9E+01	1.4E+04		1.7E-01	1.7E-01	1.4E-01	5.0E+01				
AG _{large}	173208	4.6E+03	2.7E-01	2.1E-02	9.9E-03	1.1E-02	2.9E-01	1.7E-01	5.2E+02	3.4E+01	2.9E+03	1.7E-01	2.0E-01	3.1E-01	1.8E+00	1.2E-01	9.9E+00			
AG _{large}	233001	1.6E+03	4.7E-01	7.6E-04	3.3E-04	4.4E-04	2.6E-01	2.7E-01	1.4E+03	5.3E+01	1.1E+04	3.0E-01	5.1E-01	6.2E-01	5.6E+00	2.0E-01	4.0E+01			
AG _{large}	243020	3.4E+03	3.8E-01	2.6E-02	1.5E-02	1.1E-02	3.2E-01	2.6E-01	5.5E+02	2.6E+01	7.2E+03	2.0E-01	3.2E-01	3.5E-01	1.7E+00	7.9E-02	2.2E+01			
AG _{large}	273038	3.3E+03	3.9E-01	3.2E-03	1.5E-03	1.7E-03	2.8E-01	3.8E-01	4.3E+02	4.2E+01	3.3E+03	3.9E-01	4.7E-01	5.1E-01	1.5E+00	1.5E-01	1.1E+01			
AG _{large}	4078500	1.0E+03	2.1E-01	6.3E-04	2.8E-04	3.5E-04	2.4E-01	2.5E-01		3.3E+03				6.7E-01		1.3E+01				
AG _{large}	4085427	1.3E+03	4.0E-01	1.2E-03	2.0E-04	9.9E-04	1.9E-01	6.0E-01	6.0E+02	4.6E+01	1.2E+04	5.5E-01	7.4E-01	1.0E+00	3.2E+00	2.3E-01	5.5E+01			
AG _{large}	4086600	1.5E+03	3.7E-01	7.8E-03	3.0E-04	7.5E-03	2.5E-01	3.3E-01		4.1E+01	1.0E+04		3.5E-01	6.1E-01	1.7E-01	3.6E+01				
AG _{large}	433002	2.5E+03	1.5E-01	1.2E-02	2.6E-03	9.8E-03	2.1E-01	2.3E-01	2.2E+02	1.2E+01	1.1E+03	3.2E-01	4.2E-01	4.1E-01	1.0E+00	5.4E-02	5.2E+00			

(Continues)

Table VI. (Continued)

Class	Site	A	P_{crop}	P_{water}	P_{res}	P_{lake}	Q_{mean}	CV_Q	Y_{mean} ($kg\ km^{-2}\ yr^{-1}$)				CV_Y				C_{mean} ($mg\ l^{-1}$)			
									TN	TP	TSS	TN	TP	TSS	TN	TP	TSS	TN	TP	TSS
AC _{large}	5367500	2.8E+03	2.4E-01	2.6E-02	1.3E-02	1.2E-02	2.9E-01	1.7E-01	6.1E+01	4.1E+03	2.7E-01	3.3E-01	2.1E-01	2.1E-01	1.4E+01					
AC _{large}	5368000	1.1E+03	2.9E-01	9.9E-03	1.3E-03	8.6E-03	2.8E-01	1.6E-01	5.9E+01	9.6E+03	3.6E-01	6.2E-01	2.1E-01	2.1E-01	3.4E+01					
AC _{large}	5379500	1.7E+03	3.4E-01	6.1E-04	2.3E-04	3.8E-04	2.9E-01	1.7E-01	7.0E+02	3.4E+04	1.7E-01	6.7E-01	2.5E+00	5.6E-01	1.1E+02					
AC _{large}	5382000	5.3E+03	3.2E-01	3.4E-03	1.8E-03	1.6E-03	3.1E-01	2.9E-01	4.4E+02	1.6E+04	2.8E-01	7.1E-01	1.4E+00	1.8E-01	4.8E+01					
AC _{large}	5397500	9.0E+02	2.7E-01	2.6E-03	2.3E-03	2.5E-04	2.4E-01	2.8E-01	3.3E+03	3.3E+03	4.2E-01	4.2E-01	1.3E+01	1.3E+01						
AC _{large}	5405000	1.6E+03	4.3E-01	3.7E-03	2.3E-03	1.4E-03	2.5E-01	2.7E-01	5.4E+02	1.7E+04	2.6E-01	7.0E-01	2.2E+00	2.7E-01	6.3E+01					
AC _{large}	5425500	2.5E+03	4.6E-01	1.2E-02	7.5E-03	4.9E-03	2.3E-01	3.9E-01	7.5E+02	1.1E+04	4.1E-01	5.6E-01	3.3E+00	2.7E-01	4.8E+01					
AC _{large}	5426000	2.0E+03	6.1E-01	2.3E-02	1.4E-02	9.5E-03	2.3E-01	4.7E-01	8.7E+02	1.7E+04	4.6E-01	5.9E-01	3.7E+00	3.0E-01	7.4E+01					
AC _{large}	5434500	2.7E+03	3.3E-01	1.6E-03	1.4E-03	1.7E-04	2.6E-01	3.4E-01	1.5E+03	3.1E+04	4.1E-01	7.7E-01	5.7E+00	2.5E-01	1.0E+02					
AC _{large}	573081	1.5E+03	4.4E-01	2.9E-03	2.5E-03	4.1E-04	2.3E-01	2.7E-01	5.0E+02	5.4E+01	3.1E-01	4.2E-01	2.0E+00	2.1E-01						
AC _{large}	573082	1.5E+03	4.3E-01	3.9E-03	2.5E-03	1.4E-03	2.4E-01	2.7E-01	5.0E+02	5.3E+01	3.0E-01	4.2E-01	2.0E+00	2.1E-01						
AC _{large}	603095	1.1E+03	4.5E-01	7.1E-03	5.3E-04	6.6E-03	2.3E-01	3.7E-01	7.9E+02	4.8E+01	4.4E-01	5.5E-01	3.3E+00	2.0E-01	5.8E+01					
AC _{large}	693035	5.9E+03	2.1E-01	1.6E-02	2.7E-03	1.3E-02	2.8E-01	2.8E-01	4.5E+02	3.8E+03	2.5E-01	3.9E-01	1.6E+00	8.1E-02	1.3E+01					
AC _{large}	713001	3.8E+03	4.0E-01	2.7E-02	1.4E-02	1.3E-02	3.2E-01	2.6E-01	5.5E+02	2.6E+01	2.2E-01	3.5E-01	1.7E+00	7.9E-02	3.1E+01					

A1

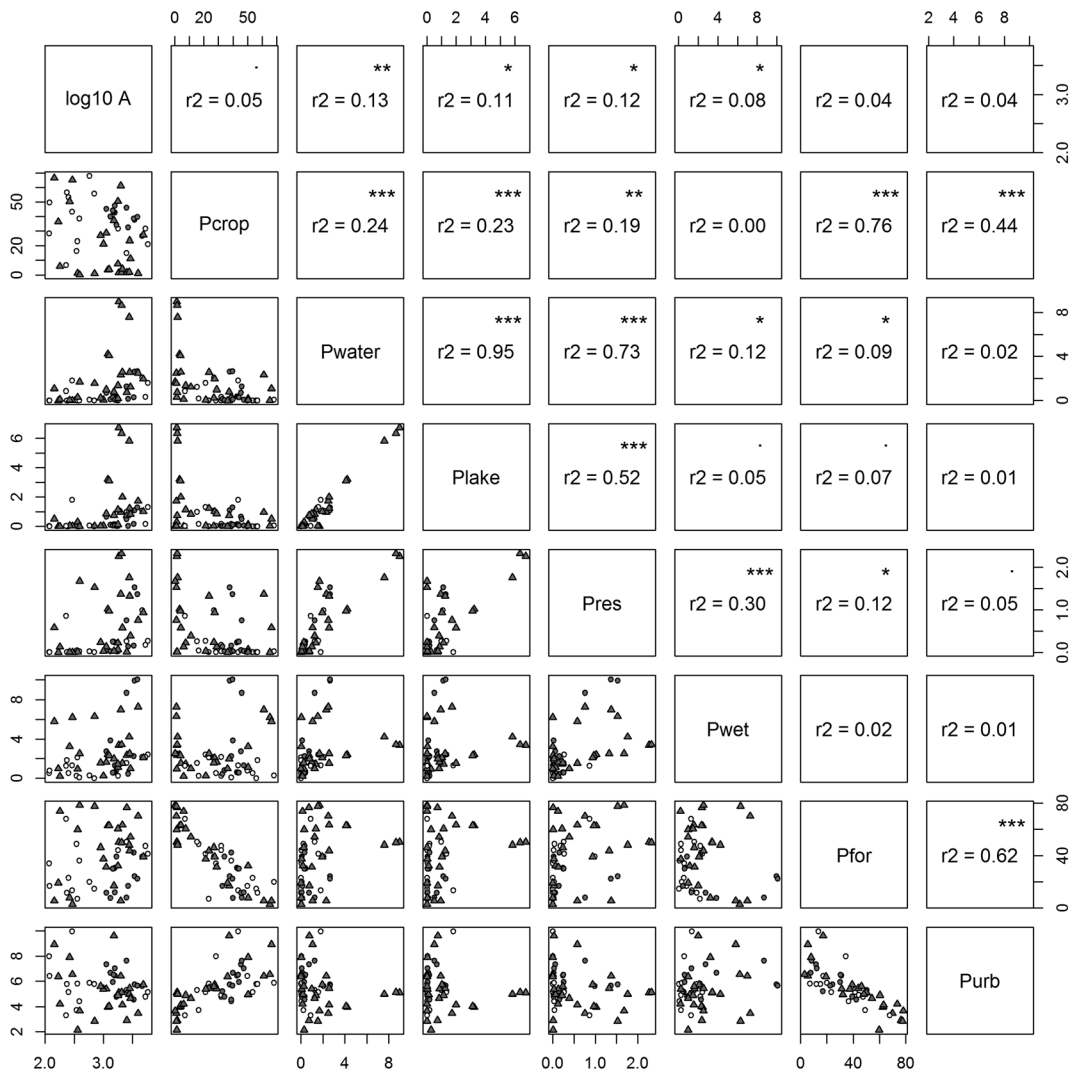


Figure A1. Correlation plots for catchment landscape characteristics. Paired correlations (r^2) are shown for all data, and stars indicate the level of significance (*, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$). Key: white circles = forested catchments (FOR), gray circles = small ($< 1000 \text{ km}^2$) agricultural catchments (AG_{small}), gray triangles = large ($> 1000 \text{ km}^2$) agricultural catchments (AG_{large})