RIVER NUTRIENT UPTAKE AND TRANSPORT ACROSS EXTREMES IN CHANNEL FORM AND DRAINAGE CHARACTERISTICS

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

(Limnology and Marine Sciences)

at the

UNIVERSITY OF WISCONSIN- MADISON

2012

Date of final oral examination: 3/20/2012

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ABSTRACT

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The overarching goal of this dissertation is to understand how ecosystem form and landscape setting dictate aquatic biogeochemical functioning and elemental transport through rivers. An emphasis is placed on understanding how wetland ecosystems influence river nutrient deliveries. Following an overview (chapter 1), I address the above goal by examining: aquatic nutrient retention in a comparative study of stream and flow-through wetland ecosystems of northern Wisconsin (chapter 2); net fluxes of inorganic and organic solutes through a mature (>100 year old) reservoir-wetland in agricultural southern Wisconsin, which was subjected to a dam removal manipulation (chapter 3); the central tendency and variability of long-term river mass export from contrasting catchments throughout the state, which spanned large gradients of terrestrial and aquatic composition (chapter 4). A synthesis of the dissertation, with particular attention to the spatial and temporal scales of study, is contained in chapter 5. Results emphasize that differences in the biogeochemical functioning of lotic vs. lentic ecosystems are linked to differences in both placement and strength of hydrologic connections.

Approved by Professor Emily H. Stanley

ACKNOWLEDGMENTS

My parents are the crucial source of inspiration, and pillar of stability, that enabled me to navigate this absurd life challenge. They are a remarkable example- the best one I know of- that good things do happen to good people, and not just by chance.

I am also deeply thankful for the stewardship of my early teachers, particularly the ones who pushed me in wonderful directions during my formative years, the most notable of which is my high school biology teacher Brother Tom Westberg.

To the friends who have witnessed my tribulations firsthand and from behind the scenes, that small handful that understands: thank you for strengthening my weaknesses, for providing affirmations when I was not so certain, and for kicking me when I needed it. Emerging studies show that victory is still possible.

For my grandparents, whose favor I still seek, that I might be a constant source of pride…

CHAPTER 1

INTRODUCTION

The overarching goal of this dissertation is to understand how ecosystem form and landscape setting dictate aquatic biogeochemical functioning and elemental transport through rivers. An emphasis is placed on understanding how wetland ecosystems influence river nutrient deliveries. The enclosed work also represents my best accomplishment, to date, toward two somewhat broader goals: increasing our understanding about the movement of water and wastes through the environment, which is a deep personal concern motivated mainly by the prospect of future conflicts involving water resources; the promotion of ecosystem ecology, for which I have an innate curiosity, and through which I hope to ensure thoughtful anticipation of the future. The enclosed research has targeted a few of the many remarkable research opportunities presented by the Wisconsin landscape. These opportunities include: the abundant wetlands of the northern forested region; the nutrient-enriched waters of the southern agricultural region; broad gradients of landscape composition in general, inter-woven with contrasting aquatic network features.

In chapter two, I examined aquatic nutrient retention in a comparative study of stream and flow-through wetland ecosystems of northern Wisconsin. The chapter was published in the journal Ecosystems in 2012 (Vol. 15, Iss. 2) with coauthors are Robert A. Johnson and Emily H. Stanley. The goal of this chapter was to understand how aquatic nutrient (nitrate) uptake rates vary among ecosystems with largely contrasting hydraulics and morphology, with a thoughtful paired experimental design that best controls for landscape-driven differences in background water chemistry. The chapter contains an application of field and modeling approaches which directly follow from my masters work (Powers et al. 2009). It also contains a detailed synthesis of existing literature, coupled with a sensitivity analysis, illustrating the contribution of different aquatic ecosystem components to whole ecosystem nutrient retention.

In chapter three, I examined net fluxes for several solute forms through a mature (>100 year old) reservoir-wetland in agricultural southern Wisconsin. The reservoir-wetland was subjected to a management manipulation, dam removal by resource managers, which altered hydraulics, channel form, and transport of nitrogen, phosphorus, and other solutes. The most noteworthy components of this chapter are the linkage to a broad management concern (aging dam infrastructure in the US), the nature of the manipulation (dam removal), and the period of record (6 years, including 3 years of baseline, dating back to my arrival in Wisconsin). The target for this chapter is the Journal of Geophysical Research: Biogeosciences. The coauthors are Jason P. Julian, Martin W. Doyle, and Emily. H. Stanley.

In chapter four, I examined the central tendency and variability of long-term river mass export from contrasting catchments of Wisconsin, which spanned large gradients of terrestrial and aquatic composition. This was a comparative study of catchment exports enabled by existing stream records, compiled mostly by the US Geological Survey, between 1986 and 2006. The goal of this chapter is to help understand how landscape characteristics, aquatic characteristics, and climate interact to influence river exports of nitrogen, phosphorus, and sediment over a broad time horizon. The target for this chapter is the journal Water Resources Research. The coauthors are Emily H. Stanley and Dale M. Robertson. A synthesis of the dissertation, with particular attention to the spatial and temporal scales of study, is contained in chapter five.

CHAPTER 2

NUTRIENT RETENTION AND THE PROBLEM OF HYDROLOGIC DISCONNECTION IN STREAMS AND WETLANDS

Abstract

Some aquatic systems have disproportionately high nutrient processing rates, and may be important to nutrient retention within river networks. However, the contribution of such biogeochemical hot spots also depends on water residence time and hydrologic connections within the system. We examined the balance of these factors in a comparative study of nitrate (NO_3^-) uptake across stream and flow-through wetland reaches of northern Wisconsin, USA. The experimental design compared NO_3^- uptake at different levels: the ecosystem level, for reaches (n=9) consisting of morphologically contrasting subreaches (*SLOW*=low mean water velocity; *REF*=reference, or higher mean water velocity); the sub-ecosystem level, for subreaches consisting of morphologically contrasting zones (*TS*=transient storage zone; *MC*=main channel zone). *SLOW* subreaches had 45% lower ecosystem-level uptake rate (K, t^{-1}) on average, indicating reduced uptake efficiency in flow-through wetlands relative to streams. The four largest K values (total n=24) also occurred in *REF* subreaches. *TS*:*MC* uptake rate varied (range=0.1-6.0), but *MC* zones consistently accounted for most NO_3^- uptake by the ecosystem. In turn, *TS* influence was limited by a tradeoff between *TS* zone uptake rate and the strength of *TS*-*MC* hydrologic connection (α or F_{med}). Additional modeling of published hydrologic parameter sets showed that strong *MC* dominance of uptake (>75% of total uptake), at the scale of solute release methods (meters to kilometers, hours to days), is common among streams and rivers. Our results emphasize that aquatic nutrient retention is the outcome of a balance involving nutrient

uptake efficiency, water residence time, and the strength of hydrologic connections between nutrient sources and sinks. This balance restricts the influence of hydrologically disconnected biota on nutrient transport, and could apply to diverse ecosystem types and sizes.

Introduction

Examinations of nutrient retention have improved our understanding of the functioning of forests [*Bormann and Likens*, 1979; *Vitousek and Reiners*, 1975], streams [*Fisher, et al.*, 1982], and also linkages between those habitats [*Valett, et al.*, 2002]. More recently, growing concern about human alterations of the global N cycle [*Vitousek, et al.*, 1997] fostered abundant N research in streams, where comparative studies across sites have been emphasized [e.g., *Mulholland, et al.*, 2009; *Webster, et al.*, 2003]. Now there is much interest in understanding the role of streams relative to other habitat types, and in patterns within the broader river network. But resulting studies have exposed a lack of empirical information for habitats that can greatly influence river network nutrient transport [*Powers, et al.*, 2009; *Tank, et al.*, 2008].

Many works point to wetlands as important sites of nutrient cycling and organic matter settling [e.g., *Jansson, et al.*, 1994], and this has contributed to a common view that wetlands function as biogeochemical hot spots within river networks. Biogeochemical hot spots possess disproportionately high nutrient reaction rates (t^{-1}) relative to the surrounding matrix [*McClain, et al.*, 2003]. While nutrient cycles in both natural and treatment wetlands are documented by a rich literature [e.g., *Kadlec and Wallace*, 2009; *Naiman and Melillo*, 1984], the ecosystem-level biogeochemical role of wetlands relative to other ecosystem types has been elucidated mostly through review and meta-analysis of separate studies [e.g., *Fisher and Acreman*, 2004; *Jordan, et al.*, 2011; *Seitzinger, et al.*, 2006] rather than direct empirical comparison. That is problematic for river network modeling because patterns aggregated across different locations and source waters could be poor representations of patterns occurring within actual river networks.

Ultimately, the contribution of different habitats to nutrient retention within river networks depends not only on nutrient processing rate, but also water residence time and hydrologic connections between nutrient sources and sinks. For example, previous research within lotic ecosystems has emphasized the biogeochemical role of transient storage or "dead" zones [*Mulholland, et al.*, 1997; *Valett, et al.*, 1997; *Valett, et al.*, 1996], which have high water residence time relative to other components of the ecosystem. Transient storage zones can be either surface features (in-channel) or subsurface features [*Briggs, et al.*, 2009; *Ensign and Doyle*, 2005; *Gucker and Boechat*, 2004], and both can be sites of rapid nutrient uptake and transformation when occupied by organic matter deposits, microbes, and algae. Nevertheless, in order for transient storage zones to contribute substantially to nutrient retention within ecosystems or river networks, these habitats must process nutrients rapidly enough to outweigh limits imposed by hydrologic disconnection from main nutrient flow.

The problem of hydrologic disconnection is not unique to biogeochemical hot spots that occur in the transient storage zone of streams. Rather, physical boundaries occur internally within many ecosystems, imposing limits to resource exchanges. For example, thermal stratification within lakes prevents mixing between surface and deep waters [*Wetzel*, 2001]. At smaller scales, low water movement in the marine benthos has been shown to reduce nutrient supply to cell boundary layers of corals [*Atkinson and Bilger*, 1992; *Thomas and Atkinson*, 1997], and even in more turbulent streams can limit nutrient transfer to benthic surfaces containing algae and microbes [*Gantzer, et al.*, 1988; *Mulholland, et al.*, 1994]. Likewise, entrainment of organic matter and fine sediments within the benthos of streams can clog interstitial spaces of substrata [*Orr, et al.*, 2009; *Schalchli*, 1992]. Thus, ecosystem components that have disproportionately high nutrient processing rates may not contribute substantially to total ecosystem retention unless so permitted by hydrologic connections.

Here we compare uptake of reactive N (nitrate) at the ecosystem level (flow-through wetlands vs. streams) and sub-ecosytem level (transient storage zones vs. main channel/thalweg zones) using experimental solute releases in contrasting systems of northern Wisconsin. We focus on two questions: A) Which systems have higher rates of nutrient uptake? B) Which systems provide the largest contribution to total nutrient retention of the reach? We propose that the contribution to nutrient retention by a nutrient sink is limited by three factors: 1) uptake efficiency within the sink; 2) residence time of the sink; 3) rate of transfer (i.e., strength of hydrologic connection) between a nutrient source and the sink. In our framework, the contribution to nutrient retention by any system is thus maximized at some optimum of those three criteria and could depend on inter-relatedness and tradeoffs among them. If present, such tradeoffs would impose constraints on nutrient processing heterogeneity within river networks, and could partly explain the observation that seemingly diverse water bodies share a similar nutrient processing rate [*Essington and Carpenter*, 2000; *Wollheim, et al.*, 2006].

Methods

Metrics and notation are shown in Table 1. We examined uptake of nitrate (NO_3^-) across morphologically diverse streams and flow-through wetlands of rural northern WI, USA. To do so, we located reaches that contained longitudinal hydrogeomorphic discontinuities, including stream flow-through wetland habitat caused by culverts, natural physiography, or beaver activity. Study reaches (118-492 m in length) contained two consecutive subreaches (38-249 m in length) and the experimental configuration is shown in Fig. 1. We compared NO_3^- uptake between contrasting habitats at two levels of organization: a) the ecosystem level, for paired subreach classes within the reach (*SLOW*=lower mean water velocity, *u*, L t^{-1}, confirmed following velocity measurement; *REF*=reference, or higher *u*); b) the sub-ecosystem level, for main channel (*MC*) and transient storage (*TS*) zones within the subreach. *MC* zones correspond to the channel thalweg and are the dominant flowpath for water and solute, whereas *TS* zones correspond to slack-water features including pools, eddies, and interstitial spaces of the benthos. Each study reach (n=9) was visited once in summer 2009 or 2010, and one of those was visited three additional times (North Cr, n=4). Land cover in the study area is predominantly temperate forest, followed by wetland and open water (lakes), while agricultural land is scarce and topography is low. Most sites had dissolved inorganic N (DIN) < 0.01 mg L^{-1}, soluble reactive P (SRP) <0.01 mg L^{-1}, and dissolved organic carbon (DOC) >5.0 mg L^{-1} (Table 2). Atomic DIN:SRP ratios were usually <15, suggesting possible N limitation. Due to a consecutive arrangement, paired *REF* and *SLOW* subreaches shared common source water, and thus had similar chemistry and discharge (*Q*, L^3 t^{-1}). The orientation of *REF*/*SLOW* subreaches (*first* or *second* in proximity to solute release point) varied among reaches. To control for photosynthetically active radiation (PAR), we targeted meadow sites with little or no riparian canopy (<10% canopy coverage).

Field methods, solute releases, and lab methods

12 short-term, multiple rate solute releases [*Demars*, 2008] of co-injected sodium chloride (NaCl) and sodium nitrate ($NaNO_3$) were conducted across paired *REF*/*SLOW* subreaches. Multiple rate solute releases are defined here as nutrient amendments caused by the

introduction of experimental solutions at distinct constant rates, altered consecutively. The goal of this approach is to achieve multiple phases of both rapidly changing and slowly changing (near steady state) nutrient enrichment conditions in the stream over a short period (hours). Experimental solute was released into study reaches using pneumatic pumps during sunny to mostly clear conditions near midday. Uptake estimates for paired subreaches were derived on the same day from a common solute release, using solute time series collected at 3 sampling stations (reach input, reach output, and boundary between subreaches). Sampling stations were positioned at well-mixed riffles, runs, culverts, or channel narrowings such that mean travel time between stations was at least 15 minutes, but usually ~30 minutes. Steady state enrichment targets at the solute release point were 10, 20, 50, and 100 μg L^{-1} above background NO_3N concentration, each lasting 30 minutes. With uptake, dilution, and dispersion of solute, this ensured enrichment levels near 10 ug L^{-1}, 20, and 50 ug L^{-1} for downstream (*second*) subreaches. Stream conditions never exceeded 120 μg L^{-1} NO_3N. For every sampling station, there were usable NO_3^- values for uptake estimation (including values at least 10 μg L^{-1} above background NO_3N at the outlet station). Recall that the order of *REF*/*SLOW* subreaches varied among reaches.

At each station, samples for Cl^- and NO_3^- time series were collected in 30 mL scintillation vials using syringes and field filtration (Whatman GF/F). For modeling purposes, solute time series were sampled over both stable and rapidly changing stages of enrichment. Specific conductivity was logged at each station using WTW meters. Prior to solute release, at least 4 Cl^-/NO_3^- samples were collected at each station. After solute arrival, at least 20 Cl^-/NO_3^- samples were collected at each station, with the exception of reach input stations (closest to pump) where less sampling was sufficient to accurately characterize the solute time series. High frequency Cl time series were constructed from Cl~specific conductivity relationships [*Gooseff and McGlynn*, 2005]. Discharge at each station was measured using one of the following: dilution gaging, velocity × area technique, mass balance technique, or culvert technique. Background ammonium-N (NH_4N), total N/P (TN/TP), total dissolved N/P (TDN/TDP), SRP, and DOC were sampled prior to each solute release. All water samples were kept on ice and in the dark following collection, then were either acidified (TN/TP, TDN/TDP) or frozen until analysis (all other analytes).

Channel surveys were conducted within 10 days following solute release. Wetted width (*w*) was measured using 9 evenly spaced transects in each subreach. Percent of total substrata and percent coverage by macrophytes were estimated visually. Substrata classes were *fines* (sediment, fine particulate organic matter), *sand*, *gravel*, *cobble*, and *coarse litter* (leaf fragments, twigs, roots). Macrophyte categories were *emergent* and *submerged*.

NO_3N (operationally, nitrate nitrogen + nitrite nitrogen) and the above N and P forms were analyzed using flow-injection analysis on an Astoria Pacific Instruments autoanalyzer (APIA). Cl was determined using a Dionex DX-500 ion chromatograph. DOC was determined using a Shimadzu carbon analyzer. Dissolved organic nutrients were estimated by difference (DON=TDN-[NO_3N+NH_4N], DOP=TDP-SRP).

Modeling and quantitative analysis

Several studies have documented differences in nutrient uptake as a function of experimental enrichment concentration [*Earl, et al.*, 2006; , 2007; *Mulholland, et al.*, 2002]. We employed multiple rate solute releases [see *Demars*, 2008] and a time series approach [see *Powers, et al.*, 2009; see *Runkel*, 2007] in order to produce NO_3N uptake estimates for a common range of low, unsaturated experimental NO_3N. In short, we used empirical information to restrict uptake calculations to an enrichment range at which the relationship between areal uptake rate (M L^{-2} T^{-1}) and nutrient concentration is approximately linear (in accordance with 1st order kinetics). This enabled an enrichment-standardized comparison of uptake between *REF*/*SLOW* subreach classes. >54 µg L^{-1} reach-centered absolute NO_3-N was our exclusion criterion (empirically determined, see Appendix A), as partial uptake saturation was sometimes detected near this enrichment level. The observation of under-saturated NO_3N kinetics below this enrichment level is supported by previous stream literature; O'Brien and Dodds [2010] reported a Michaelis-Menten half-saturation coefficient (K_s) of 67 µg L^{-1} for NO_3N uptake in prairie streams. Grimm and Fisher [1986] reported a threshold of 55 µg L^{-1} NO_3N for N limitation of stream periphyton growth.

NO_3N uptake was estimated from modeling of conservative (Cl) transport and nonconservative (NO_3N) transport using one dimensional transport (advection-dispersion) with inflow and storage model [OTIS; *Bencala and Walters*, 1983]. The model has been thoroughly described in previous works [e.g., *Runkel*, 1998; *Stream Solute Workshop*, 1990] and accounts for hydrologic gains/losses, exchange of solute between *MC* and *TS* zones, and disappearance of solute due to biotic uptake or transformation, given by:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_s - C) - \lambda C \qquad (1)$$

$$\frac{dC_s}{dt} = \alpha\frac{A}{A_s}(C - C_s) - \lambda_s C_s \qquad (2)$$

where conservative transport parameters include *D* (dispersion coefficient, L^2 t^{-1}, *A* (*C* cross-sectional area, L^2), A_s (*TS* zone cross-sectional area, L^2), α (exchange coefficient between *MC* and *TS* zones, t^{-1}) and NO_3^- uptake parameters include λ (*MC* zone uptake rate, t^{-1}) and λ_s (*TS* zone uptake rate, t^{-1}). We used multiple steps to estimate NO_3N uptake parameters (λ and λ_s).First, we used a nonlinear least squares routine (OTIS-P) to simulate conservative transport (no uptake; $\lambda = \lambda_s = 0$) of background-corrected Cl in each subreach by fitting parameters $D, A, A_s,$ and α. Second, we limited outlet NO_3^- observations to those not exceeding 54 µg L^{-1} reach-centered, absolute NO_3-N (which always retained at least 12 values following arrival of experimental NO_3^-) and used OTIS-P to fit λ and λ_s.

Mean and median water travel time owing to transient storage (F_{mean}, F_{med}^{200}) were calculated from the following relationships described in Runkel [2002]: $F_{mean}=A_s/(A+A_s)$; $F_{med}^{200}=F_{mean}\times c$, where c is $1-e^{-L\frac{\alpha}{u}}$ and L=200 m. Dahmkohler numbers (DaI, unitless), which express the degree of balance between downstream transport processes and transient storage zone processes, were calculated as $DaI=u^{-1}\times \alpha L(1+A/A_s)$.

The observed flux of surface water NO_3^- inputs (M_0, M) and simulated flux of nutrient outputs (M_x, M) were used to estimate the proportion of experimental NO_3^- inputs taken up by the ecosystem [$P=1-M_x/M_0$], and ecosystem-level first order uptake rate [$K=(u/L)\times P$]. High model uncertainty sometimes prevented simultaneous fitting of λ and λ_s, and in those instances we assumed $\lambda=\lambda_s$ in order to simulate ecosystem-level uptake metrics. Uptake velocity [$v_f=K\times$ depth] was calculated. u and depth were obtained from modeled and measured values [$u=Q/A$, depth$=A/w$]. The proportion of total mass uptake owing to uptake by the *TS* zone (P_s) was estimated [$P_s=(M_0-\hat{M}_x)/(M_0-M_x)$], where $\hat{M}_x$ (M) is a flux of nutrient outputs occurring in an OTIS simulation with no *MC* zone uptake, estimated by fixing λ to 0 and λ_s to its determined value [see *Runkel*, 2007]. Areal uptake (U, M L^{-2} t^{-1}) and uptake length (S_w, L) were calculated ($U=v_f\times C$, Sw= u/K).

Paired t-tests were used to compare differences between subreach classes (*REF*/*SLOW*, *first*/*second*) for ecosystem-level uptake (K, v_f) and hydrologic connectivity of *MC-TS* zones (α, F_{med}^{200}). Parametric paired comparisons were used for the above, except in the case of v_f which was non-normally distributed according to the Shapiro test, and instead a Wilcoxon signed rank test was used. Statistical comparisons involving λ and λ_s could not be conducted because these parameters could not always be meaningfully estimated. Data from only one North Creek 2009 date were used in the previous analyses (NC, nearest to midpoint of study season) due to potential non-independence of values at this site. In addition to rank u, alternative subreach classification criteria were considered that also express differences in the flow characteristics of streams and wetlands. Classifying paired subreaches by rank Richardson number [$Ri = g \times \text{depth} \times u^{-0.5}$, dimensionless, where g is 9.81 m^2 s^{-1}] for which a decrease indicates higher turbulence, or rank Froude number [$Fr = u \times 1/(g \times d)^{0.5}$, dimensionless] for which a decrease indicates more tranquil flow, was consistent with the classification based on rank u. Classifying paired subreaches based on rank Reynolds number [$Re = 4u \times r/v$, dimensionless, where r is the hydraulic radius, and v is kinematic viscosity assumed to be 1×10^{-6} m^2 s^{-1}] which decreases along the transition from lotic to lentic, was consistent with that of rank u, except for CI and LT.

Finally, we conducted a sensitivity analysis of P_s using published transient storage parameter sets. The published sources are listed in Appendix A (Table A) and were used for simulation of P_s in Figure 5. Some literature sources reported reach-averaged discharge (Q) but no additional discharge information, and in these instances we assumed $Q_0 = Q$ and $q_L = 0$. A few studies involving small streams did not report D or L, and in those instances only, we assumed $D = 0.1$ m^2 s^{-1} and $L = 200$ m. We then estimated two sets of P_s based on different assumptions

(λ_s:λ=1.0 , with λ=1.00e^{-4} s^{-1} and λ_s=1.00e^{-4} s^{-1}; λ_s:λ=5.0 , with λ=1.00e^{-4} s^{-1} and λ_s=5.00e^{-4} s^{-1}) using simulated releases of nonconservative solute in OTIS (discussed in methods).

Results

Hydrology and habitat

We observed large gradients of hydraulics, hydrology, and channel form. u was substantially lower in *SLOW* subreaches compared to *REF* subreaches (mean ratio=0.60; range of ratio=0.37-0.90), including two *SLOW* values <0.03 m s^{-1}, and six values <0.07 m s^{-1} (Fig. 2; see Table 3 for site abbreviations). Q and A ranged widely, from 19.2 to 194 L s^{-1}, and 0.32 to 4.3 m^2, respectively. F_{mean} ranged from 0.075 to 0.54, indicating some *TS* zones represented a substantial proportion of total stream volume. Measures of hydrologic connectivity between *TS* and *MC* zones also ranged widely (α, 2.6e^{-5} to 1.3e^{-3}; F_{med}^{200} , 0.02 to 0.38). Mean ratios of paired values (*SLOW*:*REF*) were 1.29 for α, and 3.37 for F_{med}^{200} , but these were highly variable and paired differences were not significantly different from zero. We found no significant differences between *first* and *second* subreaches for α nor F_{med}^{200} . *DaI* ranged from 0.42 to 7.0 (with two exceptions: LO *REF* subreach, 9.8; ND *SLOW* subreach, 11.9), suggesting reasonable balance between transport processes and transient storage zone processes, and reasonable transient storage parameter estimates. Substrata and aquatic vegetation varied among subreaches in relation to hydraulic gradients, and included some areas with abundant fine sediment, organic matter, and macrophytes. *Fines* dominated the substrata (median= 66%) followed by *sand* (median=25%) which together represented >70% within every subreach.

Ecosystem-level uptake

For 10 of 12 solute releases, ecosystem-level NO_3^- uptake rate (both K and v_f) were lower in *SLOW* relative to *REF* subreaches (Table 4). When limited to independent reaches shown in Fig. 2, *SLOW* subreaches had 44.7% lower K on average (n=9, p=0.008 in paired t-test). The four highest K values all occurred in *REF* subreaches (AU, ST, NA, LT). Two cases, both in *SLOW* subreaches, had no detectable uptake (LO, MU). For North Cr, visited multiple times between May 2009 and August 2009, 3 of 4 cases had both lower K and lower v_f in the *SLOW* subreach; the exception was NB, when *REF* and *SLOW* values had overlapping confidence limits (1 s.d.). For reaches shown in Fig. 2, *SLOW* subreaches had 25.3% lower v_f on average compared to *REF* subreaches (n=9, not significant). In the two reaches where v_f was larger in the *SLOW* subreach (CI and LT), depth was larger and *Re* was lower relative to the *REF* subreach. A paired *t*-test based on rank *Re* rather than rank u yielded 38.1% lower K (p=0.047) and 52.5% lower v_f (p=0.001) on average in the subreach with lower *RE*. Significant differences between paired subreaches (based on both rank u and rank *Re*) were upheld for K and v_f no matter which set of North Cr values (NA, NB, NC, or ND) were used. The *REF*/*SLOW* difference in v_f was marginally significant (p=0.09, Wilcoxon signed rank test) when all North Cr values (NA, NB, NC, ND) were used (n=12). There was no statistically significant difference between *first* and *second* subreaches for K nor v_f. The pattern of U between *REF*/*SLOW* subreaches was consistent with that of v_f due to common background NO_3N within each study reach (recall $U= v_f \times C$). Overall, subreach NO_3^- losses (P) ranged from 0 to 43.8% of experimental inputs.

Uptake by main channel and transient storage zones

NO_3^- uptake for *MC* and *TS* zones (λ and λ_s) was successfully partitioned in 12 of 22 instances with detectable NO_3^- loss. Here it is important to recognize that parameter error (1 s.d.)

for λ_s was sometimes high (error:estimate >1.0 in 6 instances). The ratio of *TS* uptake rate to *MC* uptake rate within a given subreach varied over 1 order of magnitude (λ_s:λ from 0.1 to 6.0), including several values <1.0. The highest measure of *TS* uptake rate occurred in AU (*SLOW*, λ_s=3.6e^{-4} s^{-1}), and the highest measure of *MC* uptake rate occurred in the adjacent subreach (*REF*, λ=3.0e^{-4} s^{-1}). Thus *TS* zones had a higher maximum but also a lower minimum (λ_s=1.4e^{-5} s^{-1}) relative to *MC* zones. The highest values of λ_s:λ coincided with a weak *MC-TS* hydrologic connection (α and F_{med}^{200}, Fig. 3). The ramifications of the previous pattern are demonstrated in Fig. 4. In all but one model-fitted estimate, the proportion of ecosystem-level uptake (mass) attributable to *TS* zone uptake (P_s) was <0.30. The exception was the *SLOW* subreach of AU (P_s=0.44) which had the highest reported λ_s:λ value. Note that uncertainty for *TS* uptake rate was acceptable for the highest values of λ_s:λ, α, and F_{med}^{200} that drive the distributions in Fig. 3.

Discussion

Differences in ecosystem-level uptake

The contribution of different systems to nutrient retention within river networks depends on nutrient processing rate, water residence time, and hydrologic connections between nutrient sources and sinks. Our results emphasize both the individual importance and inter-relatedness of those factors across widely contrasting system types. Further, we provide a counter example to the idea that wetlands have disproportionately high nutrient processing rates. Rather, the four highest values of ecosystem-level uptake (*K*) occurred in reference (*REF*) stream systems, which also had higher uptake rates on average when compared to lower water velocity (*SLOW*) systems (Fig. 2). This suggests lower uptake efficiency in flow-through wetlands relative to streams, for which there are at least three supporting lines of evidence. First, the pattern of lower uptake rate in *SLOW* subreaches was upheld in the temporal study element of North Creek for three of four visits that occurred in different months. Second, the pattern was not restricted to the metric K, as the magnitude of v_f was also lower for *SLOW* subreaches in all but two reaches (CI and LT); note that CI and LT had modest longitudinal contrasts for u, and were also the only reaches where Re was lower in the *REF* subreach. Third, the only two subreaches which had undetectable uptake were of the *SLOW* class, indicating flow-through wetland systems had not only lower uptake rates overall, but in some cases were clearly cold spots for NO_3^- uptake. Overall, our findings are consistent with the idea that uptake efficiency declines as water velocity slows along the transition from lotic to lentic, resulting in a tradeoff between uptake efficiency and water residence time. This tradeoff counteracts the otherwise expected pattern of increasing nutrient retention with increasing water residence time, and is likely important for wetlands and transient storage zones of streams that possess either lentic or laminar flow conditions.

Hydrologic connections within ecosystems modulate nutrient supplies to biota, and were likely important to ecosystem-level NO_3^- uptake in our study. Measures of hydrologic connectivity between *MC* and *TS* zones (α and F_{med}^{200}) ranged over one order of magnitude, while hydraulics (water velocity, shear stress, turbulence) also included diverse conditions ranging from laminar flow to turbulent flow. This included u down to 0.026 m s^{-1} and F_{med}^{200} up to 0.38, as well as stream conditions more consistent with those previously reported. The above gradients can lead to differences in local nutrient supplies to algae and microbes. For example, several studies have shown a positive effect of water motion on algal uptake of N [*Gerard*, 1982; *Parker*, 1981] and P [*Schumacher and Whitford*, 1965] which promotes transport across boundary layers of cells [*Borchardt*, 1996; *Munk and Riley*, 1952]. Also, at intermediate levels between that of the cell and the ecosystem, preferential flowpaths within surface, parafluvial, or hyporheic zones can circumvent the biota [*Kadlec and Wallace*, 2009; *Lightbody, et al.*, 2008]. This phenomenon (hydrologic "short-circuiting") was observed during pilot fluorescein (dye) releases in the *SLOW* subreach of North Cr, and is a common feature of constructed wetlands. Alternatively, the difference in *K* between *SLOW* and *REF* subreaches could be related to a difference in gross primary production [e.g., *Hall and Tank*, 2003]. However, this seems inconsistent with our results because *SLOW* subreaches often had shallow depth and abundant benthic and epiphytic algae.

Our ability to detect a difference in nutrient uptake between *REF* and *SLOW* subreaches was facilitated not only by substantial differences in hydraulic measures, but also elements of experimental design. For example, we ensured uptake estimates were associated with a low level of enrichment (<54 μg L^{-1}, reach-centered absolute NO_3N). Lack of a statistical difference between *first*/*second* subreach classes for *K* and v_f also suggests that uptake metrics were successfully standardized to a common, low range of NO_3^- enrichment. It is nonetheless important to recognize some study limitations when interpreting our findings. Given timing of the research (summer baseflow conditions), the ecosystem-level difference in *K* between *REF* and *SLOW* subreaches may not be upheld for other times of year, changing flow states in relation to precipitation or snowmelt, or longer time scales that incorporate such dynamics. Also, in-channel solute releases do not incorporate biological activity along upwelling groundwater flowpaths which have source waters external to the surface stream. Thus, some potentially important sites and times of aquatic nutrient retention are not represented in our work. However, our results are likely representative for most of the period between cessation of snowmelt and onset of leaf-fall in northern WI streams and wetlands. Candidate NO_3^- fates for our study include a) uptake by algae or microbes, b) denitrification by microbes (transformation to nitrogenous gases), and c) dissimilatory nitrate reduction to ammonium by microbes (DNRA, transformation to ammonium). Due to the short spatio-temporal scale of solute releases (meters to kilometers, hours to days) and predominance of oxygenated surface waters (main channels as well as surface transient storage zones), NO_3^- uptake here is most likely attributable to algal or microbial uptake. Finally, we stress that even when uptake efficiency is low, the biogeochemical importance of wetlands can still be realized through high water residence time (and thus total nutrient mass), through denitrification of groundwater-N, and through remineralization of organic matter stores which provide an energy source to downstream ecosystems.

Uptake by main channel and transient storage zones

TS zones encompass multiple habitat types that can serve different biogeochemical roles, but by most accounts, are commonly viewed as hot spots for nutrient uptake within rivers. Our results are not completely consistent with this view. In support, the highest recorded measure of uptake did occur in the *TS* zone (AU *SLOW* subreach, 3.6 e^{-4} s^{-1}), and the ratio of *TS*:*MC* uptake was substantial in certain cases ($\lambda_s:\lambda>5.0$ in two subreaches, Fig. 3). For comparison, McKnight and others [2004] reported uptake estimates for an Antarctic stream, including the highest value of $\lambda_s:\lambda$ we have found in the literature at this time for NO_3^- uptake (7.8). But in contrast, our results also emphasize that *TS* zones can be cold spots for uptake relative to *MC* zones ($\lambda_s:\lambda<1.0$ in 7 of 12 instances), leading to a higher range and coefficient of variation for *TS* zone uptake relative to *MC* zones. Some estimates of *TS* zone uptake rate should be interpreted with caution due to high uncertainty, which could in part reflect aggregation of modeled *TS* uptake into one rather than multiple compartments [*Briggs, et al.*, 2009]. Here, we emphasize the surface dominance of total *TS* in our sites, which in general were densely occupied by macrophytes, algae, and detritus. *SLOW* subreaches contained visually apparent surface backwaters caused by lateral (fringing) vegetation, interior ponds, and occasionally, braided channels characteristic of flow-through wetlands. Meanwhile, reaches of this study lacked coarse substrata (Table 2), and both *REF* and *SLOW* subreach classes had abundant fine sediment and organic matter deposits which can obstruct hyporheic solute exchange (*fines*>50% in 5 *REF* subreaches, and *fines*>70% in 6 *SLOW* subreaches). Also, for sites from Briggs and others [2010], the proportion of median water travel time owing to surface *TS* was >5-fold higher than that owing to hyporheic *TS*. We suspect the contribution of surface *TS* to total *TS* is important in many streams and rivers.

Zone-specific contributions to nutrient retention of the ecosystem

While the idea of biogeochemical hot spots has received much attention in recent ecological research, it is important to recognize that some hot spots do not contribute substantially to nutrient retention of whole ecosystems or river networks. For example, compared to hot spots that are hydrologically well-connected to nutrient sources, poorly connected hot spots have a diminished capacity to influence ecosystem-level nutrient retention and may not measurably alter nutrient transport. Fig. 3 also shows that for *TS* zones of streams and flow-through wetlands, high *TS* uptake rate low corresponded to low hydrologic connectivity to main channel nutrient flow (by two different measures), which in our study is probably explained by a high ratio of reactive surface area to water volume in surface *TS* zones (e.g., high coverage by macrophytes, algae, or detritus). In turn, the previous tradeoff should impose a strong restriction to the contribution of *TS* zones toward ecosystem-level nutrient retention [see *Findlay*, 1995 for a similar characterization of the hyporheic zone]; Fig. 4 confirms this expectation. In our study, *TS* zone uptake never accounted for >50% of total uptake by the ecosystem, seldom >30% (1 of

12 instances), and only sometimes >20% (4 of 12 instances). To date, few other studies have provided estimates of zone-specific mass nutrient uptake. Those revealed that *TS* zones accounted for 0.01 to 21.7 % of NO_3^- uptake in an Antarctic meltwater stream [*Runkel*, 2007], 44 to 49 % of NO_3^- uptake in a south Appalachian stream [*Thomas, et al.*, 2003], and 52 to 85% of NH_4^+ uptake in tropical headwater streams [*Gucker and Boechat*, 2004]. Recognizing uncertainty for *TS* uptake, Fig. 4 also shows that even under simulated conditions of high *TS* uptake rate (λ_s:λ=5.0, probably not a realistic expectation for most lotic ecosystems), the majority of subreaches (14 of 22) still maintained P_s <0.50. In summary, across diverse streams and flow-through wetlands of northern WI, NO_3^- uptake was either weakly dominated or strongly dominated by main channel (thalweg) mechanisms of uptake, which likely reflects biotic uptake by algal mats. Because nutrient movement is linked to water movement for both aquatic and terrestrial systems, hydrologic connections could modulate the role of biogeochemical hot spots in a broad sense.

An important question remains: How widespread is the dominance of main channel uptake across streams and rivers of the globe? Fig. 5 attempts to answer this question, which remains a subject for future research. For transient storage parameter sets compiled from the literature (Appendices A, B), we modeled two *TS* uptake scenarios: high *TS* uptake rate within the reach (λ_s:λ=5.0), and uniform uptake rate within the reach (λ_s:λ=1.0). Fig. 5A shows that under the more plausible assumption of λ_s:λ=1.0, the distribution of P_s has a high positive skew and a mean of 0.26 (P_s>0.3 in only 35% of the data sets). Based on results of this paper which show instances of λ_s:λ<1.0, we suspect Fig. 5A may still overestimate P_s in several cases. Fig. 5B shows that even under the assumption of high *TS* uptake rate at all sites (λ_s:λ=5.0), P_s has a mean of 0.46 (P_s>0.5 in 41% of the data sets). Fig. 5C shows that for a small number of systems, using either scenario, the proportion of ecosystem-level mass uptake owing to uptake in the *TS* zone (P_s) does commonly exceed 50%, and occasionally exceeds 75%. However, P_s <50% is more frequent, and many individual systems appear incapable of yielding P_s>50%. Overall, Fig. 5 provides strong evidence that the pattern of *MC* dominance is not restricted to our sites in northern WI, USA; rather it is a widespread characteristic across system sizes, regions, and *TS* zone types. This has important ramifications for river nutrient deliveries because aquatic organisms of lotic vs. lentic systems have different nutritional requirements, and decompose in a different fashion upon death.

Acknowledgements

Laboratory assistance and field assistance were provided by James Thoyre, Page Mieritz, Justin Zik, Alex Bilgri, James Sustachek, and Colleen Sylvester. Stephen Carpenter provided valuable comments on the manuscript. Work was supported by NSF funding of the North Temperate Lakes Long-term Ecological Research (LTER) Program, and State of Wisconsin Groundwater Research and Monitoring Program (project #WR07R003).

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Table 1. Metrics and notation.

Symbol	Units	Metric Name	Origin
Q	$L^3\ t^{-1}$	discharge	field measurement
w	L	mean channel width	field measurement
d	L	mean channel depth	calculation
u	$L\ t^{-1}$	mean water velocity	calculation
α	t^{-1}	exchange coefficient	OTIS parameter
D	$L^2\ t^{-1}$	dispersion coefficient	OTIS parameter
A	L^2	main channel area	OTIS parameter
A_s	L^2	transient storage zone area	OTIS parameter
F_{mean}	unitless	proportion of mean water travel time owing to transient storage	calculation
F_{med}^{200}	unitless	proportion of median water travel time owing to transient storage	calculation
DaI	unitless	Damkohler number	calculation
λ	t^{-1}	main channel decay coefficient	OTIS parameter
λ_s	t^{-1}	transient storage zone decay coefficient	OTIS parameter
K	t^{-1}	whole stream decay coefficient	calculation
v_f	$L\ t^{-1}$	uptake velocity	calculation
U	$M\ L^{-2}\ t^{-1}$	areal uptake rate	calculation
S_w	L	uptake length	calculation
P	unitless	proportion of experimental inputs taken up	calculation
P_s	unitless	proportion of experimental inputs taken up by TS zone	calculation

Table 2. Background characteristics of northern WI, USA study reaches (n=9). For North Cr (visited multiple times) only observations corresponding to Jul 18 2009 (near midpoint of study season) are included.

Metric category	Variable	Median	Range	1 s.d.
a) chemistry	Nitrate-N* (mg L^{-1})	0.007	0.004 - 0.024	0.006
	Soluble reactive P** (mg L^{-1})	0.005	0.004 - 0.018	0.004
	Ammonium-N (mg L^{-1})***	0.018	0.005 - 0.10	0.028
	Total dissolved N (mg L^{-1})	0.43	0.030 - 0.74	0.25
	Total dissolved P (mg L^{-1})	0.008	0.005 - 0.025	0.008
	Total N (mg L^{-1})	0.55	0.21 - 1.2	0.28
	Total P (mg L^{-1})	0.03	0.01 - 0.10	0.03
	DIN:SRP (atomic ratio)	10.4	4.3 - 61	17.9
	Dissolved organic carbon (mg L^{-1})	8.4	3.2 - 12	3.0
b) habitat, *ref* subreaches	% substrata as *fines*	52	24 - 99	27
	% substrata as *sand*	41	0.0 - 66	27
	% substrata as *coarse litter*	0.0	0.0 - 21	9.0
	% substrata as *gravel + cobble*	0.0	0.0 - 8.0	3.1
	% coverage by *emergent* macrophytes	18	0.0 - 51	15
	% coverage by *submerged* macrophytes	12	1.0 - 50	17
c) habitat, *slow* subreaches	% substrata as *fines*	75	5.0 - 99	30
	% substrata as *sand*	24	0.0 - 66	26
	% substrata as *coarse litter*	0.0	0.0 - 26	9.0
	% substrata as *gravel + cobble*	0.0	0.0 - 11	3.7
	% coverage by *emergent* macrophytes	31	0.0 - 86	29
	% coverage by *submerged* macrophytes	3.0	1.0 - 17	6.1

*Nitrate-N < 0.01 mg L^{-1} at all sites except LO (0.024 mg L^{-1}).

**Soluble reactive P < 0.01 mg L^{-1} at all sites except MU (0.018 mg L^{-1}).

***Ammonium-N <0.03 mg L^{-1} at all sites except LO (0.10 mg L^{-1}). Three other reaches had ammonium 0.02 - 0.03 mg L^{-1} (AL, MU, and N2).

Table 3. Hydrology and geomorphology. Measures of hydrologic connectivity between *MC-TS* zones include F_{med}^{200} (proportion of median water travel time owing to *TS*) and α. F_{mean} is mean water travel time owing to transient storage ($A_s/[A+A_s]$). Errors are 1 standard deviation from model fits.

Site Name (Abbreviation)	Date	Subreach Class	Subreach Position	Q (L s^{-1})	Water velocity (u, m s^{-1})	Width (m)	Depth (m)	F_{mean}	F_{med}^{200}	α (s^{-1})	*DaI*
Allequash Cr (AL)	Aug 27 2009	ref	first	104	0.031	11.3	0.29	0.21	0.18	3.3E-04 ± 4E-05	3.2
		slow	second	112	0.026	21.6	0.20	0.48	0.38	2.0E-04 ± 2E-05	0.9
Aurora Cr (AU)	Aug 3 2009	ref	second	23	0.056	6.2	0.07	0.34	0.27	4.5E-04 ± 4E-05	2.1
		slow	first	19	0.028	5.6	0.12	0.13	0.11	3.0E-04 ± 1E-04	3.1
Circle Lilly Cr (CI)	Jun 22 2009	ref	second	79	0.107	4.2	0.18	0.19	0.08	3.1E-04 ± 5E-05	2.3
		slow	first	77	0.075	2.7	0.38	0.15	0.10	4.3E-04 ± 5E-05	4.6
Little Tamarack Cr (LT)	Jun 1 2009	ref	first	194	0.231	6.4	0.13	0.22	0.15	1.3E-03 ± 6E-05	6.3
		slow	second	194	0.194	3.4	0.30	0.21	0.03	1.8E-04 ± 1E-04	1.1
Lost Cr (LO)	Jul 1 2009	ref	first	93	0.099	3.7	0.25	0.12	0.10	8.2E-04 ± 1E-04	9.8
		slow	second	93	0.052	5.1	0.35	0.30	0.27	6.2E-04 ± 3E-04	3.9
Muskellunge Cr (MU)	Jul 21 2010	ref	second	176	0.206	3.6	0.23	0.26	0.13	7.4E-04 ± 3E-04	2.7
		slow	first	168	0.109	9.0	0.17	0.13	0.04	2.1E-04 ± 2E-05	3.1
North Cr (NA)	May 27 2009	ref	first	83	0.139	2.9	0.21	0.11	0.04	3.3E-04 ± 4E-05	4.6
		slow	second	93	0.079	8.2	0.14	0.27	0.21	5.8E-04 ± 8E-05	6.6
North Cr (NB)	June 15 2009	ref	first	44	0.122	2.9	0.13	0.07	0.01	1.2E-04 ± 1E-05	2.7
		slow	second	51	0.070	8.2	0.09	0.25	0.19	5.1E-04 ± 7E-05	7.0
North Cr (NC)	Jul 18 2009	ref	first	60	0.117	2.6	0.19	0.15	0.02	7.8E-05 ± 2E-05	0.9
		slow	second	63	0.044	9.7	0.15	0.35	0.04	2.6E-05 ± 9E-07	0.4
North Cr (ND)	Aug 5 2009	ref	first	39	0.106	3.0	0.12	0.14	0.07	3.9E-04 ± 3E-05	5.5
		slow	second	42	0.058	9.7	0.07	0.30	0.28	8.6E-04 ± 2E-04	11.9
North Cr2 (N2)	Jul 1 2010	ref	second	89	0.134	4.3	0.16	0.13	0.06	4.0E-04 ± 1E-04	5.0
		slow	first	81	0.099	7.2	0.11	0.24	0.14	4.0E-04 ± 1E-05	1.5
Stevenson Cr (ST)	Jul 28 2009	ref	first	28	0.086	4.8	0.07	0.54	0.20	2.0E-04 ± 2E-05	0.4
		slow	second	34	0.078	7.4	0.06	0.30	0.18	3.4E-04 ± 1E-05	1.8

Table 4. Measures of nutrient uptake. Ecosystem-level uptake was partitioned into zone-level components (main channel, *MC*; transient storage, *TS*). *P* is the proportion of experimental NO_3N inputs taken up by the ecosystem. P_s is the proportion of total uptake owing to *TS* zone uptake (reported if λ_s was partitioned). Errors are 1 standard deviation from model fits.

					Ecosystem-level uptake					Zone-level uptake		
Site Name (Abbreviation)	Date	Subreach Class	Subreach Position	Background NO_3N ($mg\ L^{-1}$)	Uptake rate (K, s^{-1})	Uptake velocity (v_f, $m\ s^{-1}$)	U ($mg\ m^{-2}\ s^{-1}$)	Uptake Length (S_w, m)	P	*MC* uptake rate (λ, s^{-1})	*TS* uptake rate (λ_s, s^{-1})	P_s
Allequash Cr (AL)	Aug 27 2009	ref	first	0.006	1.6E-04 ± 3E-05	4.6E-05	3.0E-04	200	0.32	1.7E-04 ± 5E-05	1.7E-04	-
		slow	second	0.006	1.3E-04 ± 8E-06	2.6E-05	1.6E-04	198	0.27	1.4E-04 ± 4E-07	3.2E-05 ± 2E-05	0.13
Aurora Cr (AU)	Aug 3 2009	ref	second	0.005	2.7E-04 ± 7E-06	1.8E-05	9.6E-05	210	0.43	3.0E-04 ± 2E-07	1.8E-04 ± 8E-07	0.16
		slow	first	0.005	9.2E-05 ± 5E-05	1.1E-05	6.1E-05	304	0.12	6.0E-05 ± 4E-05	3.6E-04 ± 3E-04	0.44
Circle Lilly Cr (CI)	Jun 22 2009	ref	second	0.006	1.6E-04 ± 1E-04	2.8E-05	1.7E-04	664	0.22	1.6E-04 ± 6E-05	1.3E-04 ± 6E-04	0.29
		slow	first	0.006	1.6E-04 ± 8E-05	5.4E-05	3.5E-04	462	0.26	1.4E-04 ± 7E-05	3.3E-04 ± 3E-04	0.24
Little Tamarack Cr (LT)	Jun 1 2009	ref	first	0.003	1.7E-04 ± 9E-07	2.2E-05	7.5E-05	1368	0.18	1.8E-04 ± 4E-07	1.9E-05 ± 1E-06	0.03
		slow	second	0.005	1.1E-04 ± 5E-05	3.3E-05	1.6E-04	1721	0.14	1.0E-04 ± 4E-05	9.2E-05 ± 2E-04	0.15
Lost Cr (LO)	Jul 1 2009	ref	first	0.024	5.1E-05 ± 3E-05	1.3E-05	3.1E-04	1933	0.07	4.7E-05 ± 4E-05	4.7E-05	-
		slow	second	0.023	0.0	0.0	0.0	infinite	0.0	0.0	0.0	-
Muskellunge Cr (MU)	Jul 21 2010	ref	second	0.006	7.1E-05 ± 7E-05	1.7E-05	1.0E-04	2913	0.07	6.6E-05 ± 4E-05	2.3E-05 ± 2E-05	0.10
		slow	first	0.007	0.0	0.0	0.0	infinite	0.0	0.0	0.0	-
North Cr (NA)	May 27 2009	ref	first	0.010	1.8E-04 ± 3E-05	3.8E-05	3.6E-04	759	0.28	1.9E-04 ± 4E-05	1.9E-04	-
		slow	second	0.011	6.6E-05 ± 2E-05	9.4E-06	1.0E-04	1204	0.20	5.5E-05 ± 3E-05	5.5E-05	-
North Cr (NB)	June 15 2009	ref	first	0.006	6.2E-05 ± 2E-05	7.9E-06	4.7E-05	1955	0.11	4.9E-05 ± 1E-05	2.5E-04 ± 1E-04	0.24
		slow	second	0.008	7.5E-05 ± 2E-05	6.7E-06	5.1E-05	935	0.26	8.2E-05 ± 2E-05	1.4E-05 ± 4E-05	0.05
North Cr (NC)	Jul 18 2009	ref	first	0.005	9.1E-05 ± 3E-05	1.8E-05	8.0E-05	1287	0.16	8.8E-05 ± 3E-05	8.8E-05	-
		slow	second	0.007	8.0E-05 ± 9E-06	1.2E-05	8.2E-05	548	0.44	9.1E-05 ± 2E-05	9.1E-05	-
North Cr (ND)	Aug 5 2009	ref	first	0.008	1.1E-04 ± 2E-05	1.3E-05	1.0E-04	976	0.22	1.1E-04 ± 3E-08	6.6E-05 ± 1E-04	0.07
		slow	second	0.010	9.6E-05 ± 5E-06	7.1E-06	7.4E-05	606	0.40	9.0E-05 ± 8E-06	9.0E-05	-
North Cr2 (N2)	Jul 1 2010	ref	second	0.009	1.5E-04 ± 4E-05	2.3E-05	2.0E-04	924	0.23	1.4E-04 ± 5E-05	1.4E-04	-
		slow	first	0.008	5.9E-05 ± 6E-05	6.7E-06	5.0E-05	1674	0.06	4.9E-05 ± 7E-05	4.9E-05	-
Stevenson Cr (ST)	Jul 28 2009	ref	first	0.006	2.1E-04 ± 5E-05	1.4E-05	7.8E-05	421	0.24	1.2E-04 ± 4E-05	1.7E-04 ± 2E-04	0.15
		slow	second	0.005	8.9E-05 ± 9E-06	5.2E-06	2.4E-05	880	0.15	7.0E-05 ± 1E-05	7.0E-05	-

Figure Legends

Figure 1. Experimental configuration and morphology of study reaches. Study reaches consist of paired subreaches, including reference (*REF*) and low water velocity (*SLOW*) categories. Note that the order of *REF* and *SLOW* subreaches varied among sites (see Table 3). Subreaches consist of main channel (*MC*) and surface transient storage (*TS*) zones. The aerial photo is the North Cr site. Square symbols are road culverts. Dotted line is wetted width.

Figure 2. NO_3N uptake for paired reference (*REF*) and lower water velocity (*SLOW*) subreaches of northern Wisconsin streams and flow-through wetlands. Dark gray= reference subreaches (*REF*). Light gray= low water velocity subreaches (*SLOW*). The relative magnitude (rank) of mean velocity (u) was used to classify *REF* vs. *SLOW* subreaches, and the mean difference in K between *REF* and *SLOW* subreaches is significant (6.57 e^{-5} s^{-1} lower, or 44.7%, in *SLOW*; p=0.008). Two of three additional visits to North Cr between May and August 2009 (not independent, not shown) also had lower K in the *SLOW* subreach. Boxplot whiskers are 1.5×interquartile range.

Figure 3. Transient storage (*TS*) zone nutrient uptake rate and the strength of hydrologic connection to main nutrient flow. Two different measures of hydrologic connectivity between *TS* and main channel (*MC*) zones are provided: α (exchange rate between *MC* and *TS* zones, t^{-1}), and F_{med}^{200} (proportion of median water travel time owing *TS* zone storage, unit-less). λ_s:λ is the rate of *TS* uptake relative to *MC* uptake for a given subreach. Uncircled=low water velocity subreaches (*SLOW*). Circles=reference (higher water velocity) subreaches (*REF*). Dashed lines are the negative exponential fits ($y \sim a^*e^{-bx}$) with a=6.0.

Figure 4. Contribution of transient storage (*TS*) zones to total NO_3N uptake for northern Wisconsin streams and flow-through wetlands. P_s is defined as the proportion of ecosystem-level

mass uptake owing to uptake in the *TS* zone. For subreaches in which uptake was detectable (n=22), P_s values were simulated based on two alternative assumptions (balanced *TS* uptake rate, λ_s:λ=1.0, circles; high *TS* uptake rate, λ_s:λ=5.0, triangles). For group A (left), model-fitted P_s estimates were available from partitioned estimates of λ_s and λ (bars). For group B, model-fitted estimates were not available (ordered by circle height).

Figure 5. Simulated contribution of transient storage (*TS*) zones to total nutrient uptake for streams, rivers, and flow-through wetlands from published studies. *TS* parameter sets were compiled from the literature (n=290, Appendices A and B) to simulate P_s (proportion of ecosystem-level mass uptake owing to uptake by the *TS* zone). Two different P_s estimates are provided for each data set: panel A, balanced *TS* uptake rate (λ_s:λ=1.0) which corresponds to a reasonable estimate of P_s for most streams and rivers; panel B, high *TS* uptake rate (λ_s:λ=5.0) which corresponds to an upper bound of *Ps* for most streams and rivers). Panel C shows an inter-site comparison of P_s from above. Flow-through wetland (*WE*) sites were so described by the authors, and each had mean water velocity <0.06 m s^{-1}. We propose three additional classes of lotic ecosystems that are grouped to the right of *WE* sites: 1) *TS dominant* (left), contribution to ecosystem-level nutrient retention (P_s) trends >0.5 regardless of uptake scenario; 2) *TS sensitive* (center), P_s trends >0.5 for high *TS* uptake rate only; 3) *MC dominant* (right), P_s trends <0.5 regardless of uptake scenario. Note that systems of the *TS dominant* class are known to have large hyporheic zones. Boxplot whiskers are 1.5×interquartile range for available data in each group, some of which include replication in time or space. Site codes refer to streams and rivers located in USA unless otherwise indicated: WE (flow-through wetland sites), SY (Sycamore Cr, AZ), GR (Green Cr, Antarctica), AN (streams of Andrews Experimental Forest, OR), IN (Indian Cr, PA), HF (streams of Hubbard Brook Experimental Forest, NH, excluding Hubbard Brook

and Bear Brook), GC (Goodwin Cr, MS), LL (Little Lost Man Cr, CA), PA (Pajaro R, CA), GA (Gallina Cr, NM), PI (Pinal Cr, AZ), LR (large rivers from Cheong and Seo 2003, including Mississippi R and Missouri R), BB (Bear Brook, NH), CO (streams at Coweeta Hydrologic Laboratory, VA), HB (Hubbard Brook, NH), SK (St. Kevin Gulch, CO), UV (Uvas Cr, CA), SN (Snake R, CO), WB (West Fork Walker Branch, TN), SP (streams and rivers of Spain), GE (streams of Germany), WI (streams of southern WI). Remaining P_s values, each from sites with n<3 sets of *TS* parameters, are plotted together as one group (other, OT).

Figure 1.

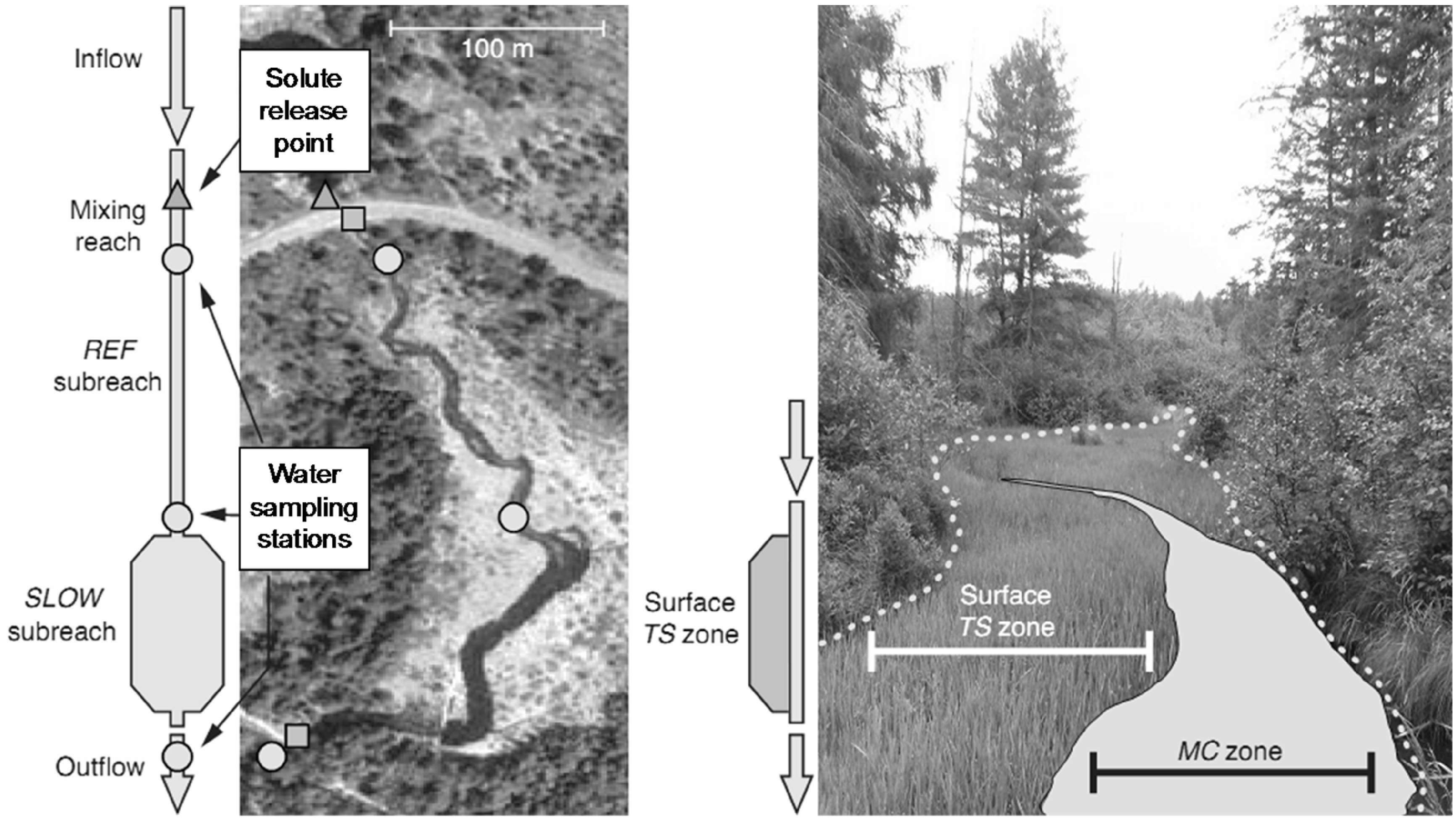

Inflow
Mixing reach
REF subreach
SLOW subreach
Outflow
Solute release point
Water sampling stations
100 m
Surface TS zone
Surface TS zone
MC zone

Figure 2.

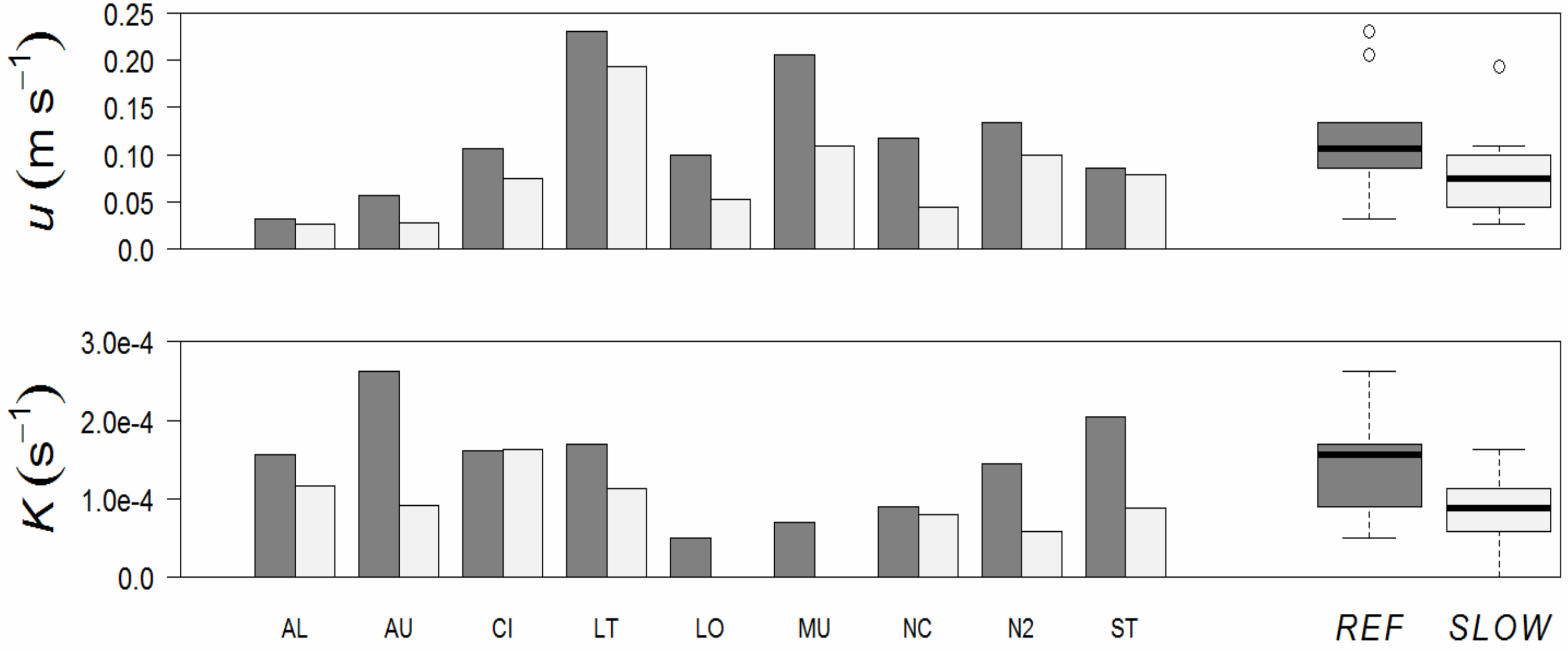
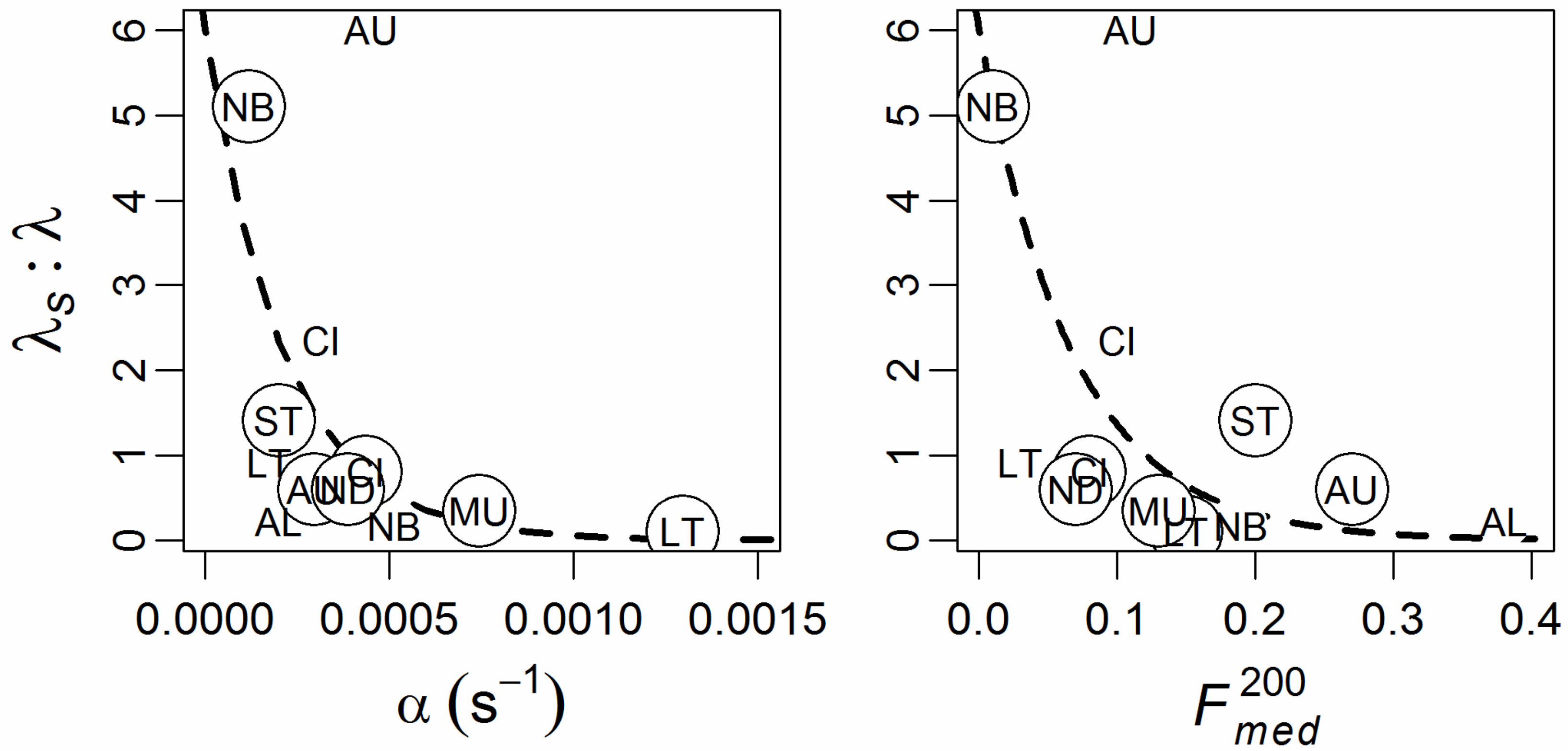

u (m s^{-1})
0.25
0.20
0.15
0.10
0.05
0.0
K (s^{-1})
3.0e-4
2.0e-4
1.0e-4
0.0
AL
AU
CI
LT
LO
MU
NC
N2
ST
REF
SLOW

Figure 3.


$\lambda_s : \lambda$
0
1
2
3
4
5
6
AU
NB
CI
ST
LT
AU
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AL
NB
MU
LT
0.0000
0.0005
0.0010
0.0015
$\alpha\ (s^{-1})$
AU
NB
CI
ST
LT
CI
ND
AU
MU
LT
NB
AL
0.0
0.1
0.2
0.3
0.4
F_{med}^{200}

Figure 4.

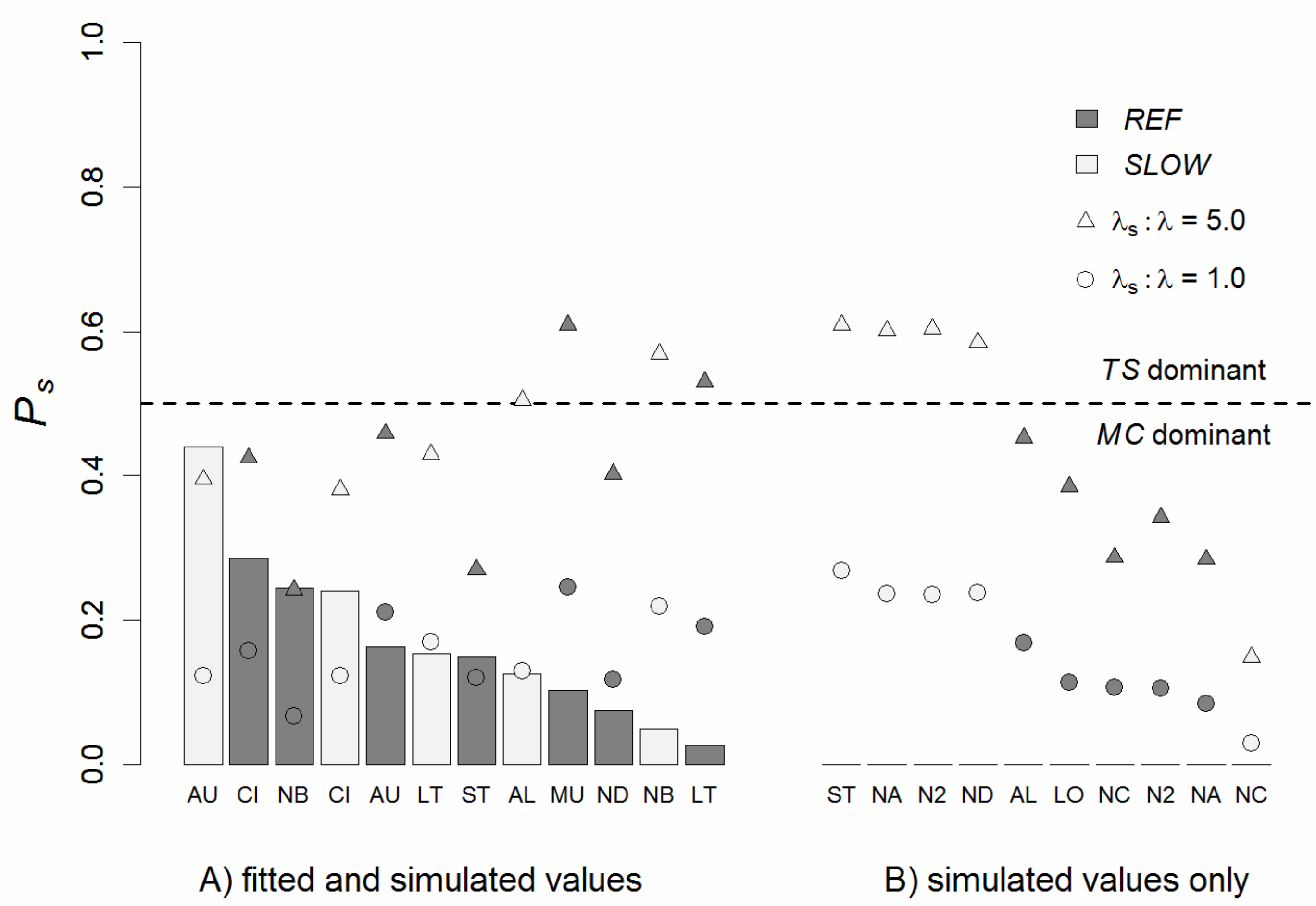
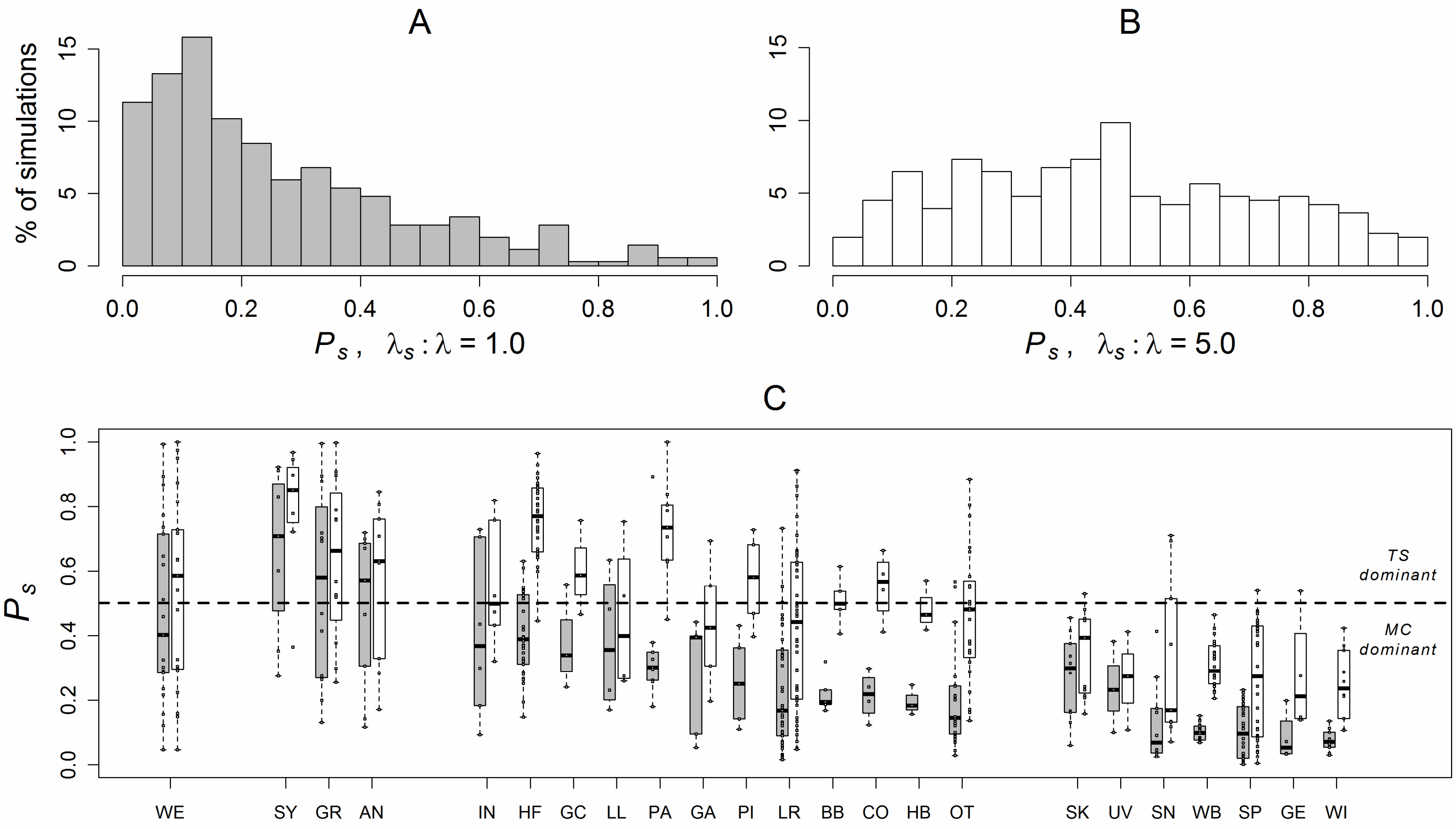

P_s
0.0
0.2
0.4
0.6
0.8
1.0
REF
SLOW
$\lambda_s : \lambda = 5.0$
$\lambda_s : \lambda = 1.0$
TS dominant
MC dominant
AU CI NB CI AU LT ST AL MU ND NB LT
ST NA N2 ND AL LO NC N2 NA NC
A) fitted and simulated values
B) simulated values only

Figure 5.


A
B
% of simulations
15
10
5
0
0.0
0.2
0.4
0.6
0.8
1.0
P_s, $\lambda_s : \lambda = 1.0$
P_s, $\lambda_s : \lambda = 5.0$
C
P_s
1.0
0.8
0.6
0.4
0.2
0.0
TS dominant
MC dominant
WE
SY
GR
AN
IN
HF
GC
LL
PA
GA
PI
LR
BB
CO
HB
OT
SK
UV
SN
WB
SP
GE
WI

Appendix A. Expanded nutrient release methods

As described in the methods, NO_3N uptake was estimated from modeling of conservative (Cl) transport and nonconservative (NO_3N) transport using one dimensional transport (advection-dispersion) with inflow and storage model [OTIS; *Bencala and Walters*, 1983]. The below steps enabled interpretation of uptake saturation patterns for the center of each subreach, which are more representative and comparable across sites than patterns occurring at subreach inlets or outlets. First, we used OTIS to simulate conservative transport (no uptake; $\lambda = \lambda_s = 0$) of background-corrected Cl in each subreach by fitting parameters $D, A, A_s,$ and α. This yielded a simulated time series of background-corrected Cl for the subreach outlet. We next simulated a time series of background-corrected Cl for the subreach midpoint (in terms of water travel time) using fitted conservative transport parameters. The ratio of $Cl_{max,centroid}$:$Cl_{max,outlet}$ was calculated for use below. This ratio (*r*) mostly reflects dilution because maximum Cl occurred near steady state enrichment conditions (often, a true steady state was achieved), and did not exceed 1.3 in any subreach. Then, prior to fitting λ and λ_s, we tested for a decline in nutrient uptake at excess NO_3N concentration that was plausible based on biogeochemical theory. To do so, we first simulated an "expected" time series of background-corrected NO_3N at the outlet (C_{exp}) under conditions of no uptake ($\lambda = \lambda_s = 0$). We next simulated a time series of approximate concentration-specific uptake rates (λ_c), for each NO_3N observation based on:

$$\lambda_C = \left(1 - \frac{C_{obs}}{C_{\exp}}\right) * \frac{u}{L} \tag{1}$$

where C_{obs} is observed background-corrected NO_3N, *u* is mean water velocity, and *L* is reach length. Then we statistically tested for declines in λ_c with increasing absolute NO_3N. This involved Bayesian analysis of change points (statistical package *bcp* in platform *R*) which detects a change in mean uptake ($\bar{\lambda}_C$) over the range of C_{obs}. Results from Bayesian analysis of change points were consistent with patterns visible by eye: in some cases, no decline in λ_c was observed at excess NO3N, while in others, λ_c declined above an enrichment threshold (C_p). Note that there was not a substantial change in the pattern λ_c~C_{obs} pattern when restricted to C_{obs} occurring at or near steady state enrichment, so we used the entire time series of λ_c~C_{obs} in this step. This approach enabled detection of partial saturating patterns that, in the absence of data at very high nutrient enrichment, cannot always be parameterized effectively using conventional saturation approaches (e.g., Michaelis-Menten). Of 24 λ_c time series, 12 had a detectable change consistent with partial saturation, while 12 had no evidence of change. We then calculated C_{thresh}, a reach-centered enrichment threshold at which λ_c declines, based on the exponential decay function:

$$C_{thresh} = C_{cp} * \frac{1}{e^{-\bar{\lambda}_C \tau_{50}}} * r + C_{bg} \tag{2}$$

where C_{cp} is the threshold NO3N concentration determined from change point analysis, $\bar{\lambda}_C$ is the mean of λ_c corresponding to <C_{cp} (an approximation of uptake rate, used for this step only), τ_{50} (T) is half of mean water residence time $\left(\frac{L}{2u}\right)$ for the reach, r is a dilution-dispersion correction from above, and C_{bg} is background NO3N. Mean C_{thresh} was 54 µg L^{-1} (± 21, 1 s.d.). We next isolated unsaturated portions of each outlet NO3N time series based on the common criterion of <54 µg L^{-1} absolute NO3N. To do this for each subreach, we calculated C_{test} by substituting each individual value of C_{obs} in place C_{cp} given by equation 2. C_{obs} values resulting in C_{test} > 54 µg L^{-1} were then discarded, yielding the time series C_{use} which always had at least 12 values following initial arrival of experimental NO3N. The observation of under-saturated NO3N kinetics below this enrichment level is supported by previous stream literature; O'Brien and Dodds [2010] reported a Michaelis-Menten half-saturation coefficient (K_s) of 67 µg L^{-1} for NO3N uptake in prairie streams. Grimm and Fisher [1986] reported a threshold of 55 μg L^{-1} NO_3N for N limitation of stream periphyton growth. Finally, we estimated NO_3N uptake parameters (λ and λ_s) using the entire time series of background-corrected NO_3N for the inlet, and C_{use} for the outlet.

Literature sources for transient storage parameter data sets, used for modeling of P_s in Figure 5, are shown in Table A.

Table A. Literature sources for transient storage parameter data sets used for modeling of P_s in Figure 5. Systems are located in USA unless otherwise noted. Abbreviations: R=river, Cr= creek, Br= brook.

Reference	System(s)
Argerich and others (2008)	Riera de Santa Fe, Spain (SP)
Bencala (1984)	Little Lost Man Cr, California (CA)
Bencala and Walters (1983)	Uvas Cr, CA
Bencala and others (1990)	Snake R, Colorado (CO)
Broshears and others (1993)	St. Kevin Gulch, CO
Broshears and others (1996)	St. Kevin Gulch, CO
Butturini and Sabater (1999)	Riera Major, SP
Chapra and Wilcock (2000)	Paiko R*, New Zealand (NZ)
Cheong and Seo (2003)	Amite R, Louisiana (LA); Antietam Cr, Maryland (MD); Bayou Ancoco, LA; Bayou Bartholomew, LA; Bear Cr, CO; Chatahoochee R, Georgia (GA); Clinch R, Virginia (VA); Coachechella Canal, CA; Comite R, LA; Conococheague Cr, MD; Copper Cr, VA; Difficult Run, VA; Green and Duwamish R, Washington (WA); Little Pincy Cr, MD; Monocacy R, MD; Missouri R (MT); Mississippi R, LA; Powell R, Tennessee (TN); Red R, LA; Sabin R, Texas (TX); Salt Cr, Nebraska (NE); Tangipahoe R, LA; Tickfau R, LA
D'Angelo and others (1993)	streams of Coweeta Hydrologic Laboratory, Virginia (VA)
Fernald and others (2001)	Willamette R, Oregon (OR)

Reference	System(s)
Ge and Boufadel (2006)	Indian Cr, Pennsylvania (PA)
Gooseff and others (2004)	Green Cr, Antarctica
Gücker and Pusch (2006)	Denmitzer Mill Br, Germany (GE); Erpe, GE
Hall and others (2002)	streams of Hubbard Brook Experimental Forest, New Hampshire (NH)
Hart and others (1999)	West Fork Walker Branch, TN
Harvey and others (1996)	St. Kevin Gulch, CO
Harvey and others (2003)	Pinal Cr, Arizona (AZ)
Harvey and others (2005)	Shark River Slough, Florida (FL)
Keefe and others (2004)	constructed wetlands* near Phoenix, AZ
Kimball and others (1994)	St. Kevin Gulch
Martí and others (1997)	Sycamore Cr, AZ
Martinez and Wise (2003)	Orlando Easterly Wetland*, FL
McKnight and others (2002)	Snake R, CO
McKnight and others (2004)	Green Cr, Antarctica
Morrice and others (1997)	Aspen Cr, New Mexico (NM); Rio Calaveras, NM; Galina Cr, NM

Reference	System(s)
Mulholland and others (1997)	High White Cr, TN; West Fork Walker Branch, TN
Powers and others (2009)	streams of southern Wisconsin (WI)
Ruehl and others (2006)	Pajaro R, CA
Stofleth and others (2008)	Little Topshaw Cr, Mississippi (MS); Goodwin Cr*, MS
Webster and others (2003)	Ball Cr, North Carolina (NC); Bear Br, NH; E1 outlet, Alaska (AK); Eagle Cr, MI; East Fork Little Miami R, Ohio (OH); Gallina Cr, NM; Kings Cr, Kansas (KS); Mack Cr, OR; Quebrada Bisley, Puerto Rico; Sycamore Cr, AZ; West Fork Walker Branch, TN
Valett and others (1997)	Aspen Cr (NM); Rio Calaveras (NM); Gallina Cr (NM)
Wondzell and others (2006)	streams of Andrews Experimental Forest, OR

*Wetland site, per description of the authors. These sites all had mean water velocity <0.06 m s^{-1}.

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CHAPTER 3

ALTERED STREAM CHEMISTRY FOLLOWING THE LOSS OF A MATURE AGRICULTURAL IMPOUNDMENT

Abstract

A remarkable number of small impoundments exist globally. Many of these artificial water bodies are well-positioned to influence riverine transport of fertilizing nutrients, sediment, and toxins. However, small impoundments are also vulnerable to structural and functional changes as they age, due to sedimentation. Despite potential biogeochemical importance, the influence of small impoundments on solute transport and transformation remains poorly understood, especially for mature systems. We examined the biogeochemical role of a mature (>100 year old) run-of-river impoundment in agricultural Wisconsin, USA. To do so, we measured instantaneous net fluxes of inorganic and organic solutes through a study reach that bounded the impoundment, including 3-yr before and 3-yr following dewatering and removal of a small dam. Prior to manipulation (reservoir-wetland state), the impoundment was a persistent net sink for sulfate, and during the warm season only, a net sink for nitrate as well as ammonium. Following manipulation, mean wetted width and mean water travel time decreased from 20.0 to 8.0 m and 4.0 to 1.5 hrs, shifting from lentic to lotic conditions. Consistent with predictions based on reduced water travel time only, either the magnitude or variability (CV) of instantaneous net solute fluxes were reduced for every measured solute form except chloride, including nitrate, sulfate, soluble reactive phosphorus (P), dissolved organic nitrogen (N), and dissolved organic P. Autoregressive modeling of solute input/output time series indicated a short-term release of ammonium from the study reach during the first year post-manipulation, and thereafter, a reduction in net retention of nitrate, sulfate, and ammonium. A pre-manipulation relationship between sulfate and nitrate retention was also absent post-manipulation. Our results emphasize the biogeochemical importance of reservoir-wetlands, which are increasing in global surface coverage and should be considered in the management of dams and surface water pollution.

1. Introduction

In recent years, it has become clear that a remarkable number of small, artificial water bodies occur in agricultural and suburban landscapes. Between 3 and 8 million water bodies exist in the US alone [*Doyle and Havlick*, 2009; *Renwick, et al.*, 2005b], and many are thought to be small artificial impoundments with surface area <1 km^2. These systems intercept a large quantity of runoff and material exported from upslope terrestrial and aquatic systems, and promote long-term storage of sediment in North America [*Renwick, et al.*, 2005b]. Because high impoundment densities occur in agricultural areas such as the Midwestern grainbelt [*Downing, et al.*, 2006; *Smith, et al.*, 2002] many impoundments are also well-positioned to influence riverine transport of fertilizing nutrients, sediment, and toxins that dictate surface water quality.

To date, most biogeochemical studies of impoundments focus on large, long-lived systems [e.g., *Kelly*, 2001; *O'Keeffe, et al.*, 1990]. Yet, relative to larger systems, small impoundments are far more numerous, have a comparable global surface area [*Downing, et al.*, 2006], and are more susceptible to failure [*Evans, et al.*, 2000] or removal [*Ahearn and Dahlgren*, 2005; *Doyle, et al.*, 2005; *Stanley and Doyle*, 2003]. Limnological principles also suggest that due to shallower depth, small impoundments should function differently than deeper lakes and reservoirs. This expectation has been verified in recent research. For example, a global analysis by Harrison et al. (2009) showed that N-removal efficiency of reservoirs was nearly one order of magnitude higher compared to natural lakes, with highest efficiency in smaller reservoirs. Of a modest number of studies involving small impoundment biogeochemistry [e.g., *Fairchild and Velinsky*, 2006; *McIntyre*, 1993; *Nowlin, et al.*, 2005], few have targeted mature, sediment-filled impoundments which foreshadow the trajectory for numerous other systems.

During impoundment maturation, sedimentation sometimes progresses rapidly [*Graf, et al.*, 2010; *Renwick, et al.*, 2005a] and is a major concern for reservoir management. For example, Downing et al. [2008] reported water storage losses of 0.4-11.0% annually for small impoundments (<1 km^2) of Iowa, USA. Others observed similarly rapid rates of water storage loss [*Dendy*, 1968; *McHenry*, 1974] and some systems have already lost the majority of water storage capacity [*Hargrove, et al.*, 2010; *Minear and Kondolf*, 2009]. The initial effects of impoundment sedimentation are usually most apparent near inlets, where shallow depth promotes the establishment of wetlands, especially in regions of modest relief [*Kalff*, 2002] such as the Midwestern US. Thus, the process of impoundment sedimentation can produce hybrid ecosystems with wetland charactereristics that expands over time. We refer to such ecosystems as reservoir-wetlands. Reservoir-wetlands share design features of treatment wetlands including shallow depth, accumulations of particulate organic matter, and abundant emergent vegetation or biofilms [*Kadlec, et al.*, 2005] and so too could be important sites of biological uptake and transformation of aquatic nutrients. Many reservoir-wetlands also differ from isolated wetlands and drainage wetlands in that they intercept substantial inputs of water and nutrients that would otherwise be delivered to downstream aquatic ecosystems. Barring intervention, the contribution to global wetland coverage by impoundments will increase as they age and fill with sediment, and this could be an important consideration for future water quality and wetland management.

Resolving the biogeochemical role of small impoundments will require a combination of remotely sensed information over a broad extent, and site-specific information about ecosystem functioning. Here, we focus on the latter by considering a 6-year period of record for net fluxes of inorganic and organic solutes through a mature (>100 year old) run-of-river impoundment in agricultural central Wisconsin. At the onset of the study, the system was a reservoir-wetland ecosystem with balanced annual inputs and outputs of sediment. We then used a management manipulation- incremental dewatering and removal of a small dam (resulting in hydrogeomorphic alteration)- to evaluate likely changes in the biogeochemical role of the ecosystem. Hydraulic characteristics such as mean water residence time greatly influence aquatic nutrient budgets, and can be important design features of treatment wetlands [*Jenkins and Greenway*, 2005; *Martinez and Wise*, 2003a; *Persson, et al.*, 1999]. We posited that if hydraulics strongly dictates net solute fluxes, then a manipulated reduction in mean water residence time should increase the similarity between input/output (surface water) time series; this would shift instantaneous net fluxes within the ecosystem toward balanced mass, and also reduce their temporal variability. Alternatively, factors in addition to hydraulics- such as altered solute uptake efficiency, or mobilization of novel solute pools- must be important if any other type of change in net flux occurs (increase in magnitude; sign reversal; increase in temporal variability).

2. Methods

2.1 Site Description

Site selection was prompted by a planned removal of the 100+ year-old, 5.4 m tall Big Spring dam (hydraulic height= 3.4 m) on Big Spring Creek, WI (43°40′10.92″N, 89°38′53.88″W) by resource managers. We used a 1.4 km study reach that bounded the entire impoundment (Fig. 1), which had surface area of 0.028 km^2 and contributing area of 20 km^2. Prior to dam removal, the study reach was a mature reservoir-wetland, which at the dam had accumulated 2.5 m of benthic sediment and organic matter. The sediment budget was variable but approximately balanced during the pre-manipulation phase (mean instantaneous net retention of total suspended sediment (TSS) = 0.008 ± 0.49 s.d., as a proportion of inputs; n=28 observations). The catchment of Big Spring Creek is a groundwater-dominated system with abundant springs, sandy soils, low relief, and low drainage density. One large perennial spring contributes the majority of surface water inputs to the study reach and stabilizes the flow regime. As a consequence, baseflows supply most of the annual water yield, and runoff periods are abbreviated. The catchment contains remnant forest patches, but mostly consists of corn crop and pasture land. Stream dissolved inorganic nitrogen is high (background NO_3-N= 2-3 mg L^{-1}, Table 1), and mean baseflow discharge (Q) entering through the mainstem of the study reach is 0.27 m^3 s^{-1}. The study reach lacked canopy cover over the majority of its length [*Julian, et al.*, 2010].

2.2 Experimental Sequence

The Big Spring management manipulation involved incremental dewatering in 5 phases during summer 2008, which caused a gradual channelization of the study reach. This began with the removal of one 0.3 m flashboard in July 2008, and proceeded with subsequent notching of dam concrete at two week intervals between July 2008 and September 2008. All remaining dam infrastructure was removed by September 2008. Between fall 2008 and spring 2009, two sections of the study reach (each < 100 m) were re-routed into restored channel meanders. Planning information associated with the dam removal may be obtained from the Wisconsin Office of Dam Safety, the Wisconsin River Alliance, or Inter-fluve Inc.

2.3 Study Design

We evaluated solute transport through the study reach over a 6 yr period of record, including 3+ yr prior to manipulation (reservoir-wetland state). To do so, we took repeated measures of inorganic solute (chloride; nitrate; ammonium; sulfate; soluble reactive phosphorus, SRP) and organic solute (dissolved organic N, DON; dissolved organic P, DOP). Solute was collected at multiple water sampling stations including: one primary output station located 100 m downstream of the dam site, one primary upstream/input station located 1.4 km upstream of dam site (near the former reservoir inlet), and additional secondary stations used for characterization of minor tributary or spring inputs. For the transitional period of 2008, which involved phased management interventions, we sampled during periods of quasi-equilibrium only (>7 days following each management intervention).

To examine possible changes in the biogeochemical role of the study reach following manipulation, we first used intervention analysis of input/output time series for solute concentration. Next, to examine the possibility of linked biogeochemical processes, we tested for statistical relationships between solute forms. We then estimated instantaneous net solute fluxes, and evaluated these with descriptive analysis. A stable flow regime, caused by a large perennial spring upstream of the study reach, facilitated flux estimation throughout the study. Hydrogeomorphic measures, which can influence biogeochemical budgets, were also measured.

2.4 Analysis of Solute Concentration Time Series

We used intervention analysis [*Box and Tiao*, 1975] to test for changes in solute concentration due to manipulation. Detailed modeling methods, as well as model diagnostics, are contained in Appendix B. Our response variable (Y, mg L^{-1}) was

$$Y = C_O - C_I \qquad \text{(Eq. 1)}$$

where C_O is a time series of solute concentration at the primary output or “treatment” station, and C_I is the time series of solute concentration at the primary input or “reference” station. A similar statistical approach has been used in previous whole ecosystem manipulation experiments, in which time series from the manipulated system are compared to corresponding time series from a reference (not manipulated) system [*Carpenter, et al.*, 1989]. Y was consistently autocorrelated at lag 1, but not at higher lags by the Durbin-Watson test. A time series with lag 1 autoregressive structure, along with experimental effects, may be expressed in the general form

$$Y = B_0 + \phi Y_{t-1} + \sum_i^n M_i D_i + e_t \qquad \text{(Eq. 2)}$$

where B_0 is the intercept parameter, Y is the differenced time series (C_O-C_I), ϕ is an autoregressive parameter, M_i is a vector of model coefficients employed by dummy variables D_i (0's to indicate the pre-manipulation phase, 1's to indicate 1 or more post-manipulation phases), and e_t is a time series of independent, normally-distributed residuals.

For each solute form, we selected the most parsimonious stationary model using AIC [*Burnham and Anderson*, 2002]) from 4 different candidate models (Table 2):

1) Null; no change following manipulation (intercept parameter B_0 only);
2) Simple effect; one-step change following manipulation (intercept parameter B_0, plus parameter M_{simple} for changes incurred following manipulation);
3) Seasonal effect; season-specific change following manipulation (intercept parameter B_0, plus parameter M_{warm} for post-manipulation changes incurred during the warm season defined as May 15 to Sep 15, and M_{cool} for post-manipulation changes incurred during the remainder of the year);
4) Annual effect; year-specific change following manipulation (intercept parameter B_0, plus parameter M_{year1} for post-manipulation changes incurred up to the end of 2009, and M_{year2} for post-manipulation changes incurred in 2010).

Parameter values, standard errors, and *p*-values were estimated for the best model of each solute form. M_i units are mg L^{-1}, such that M_i=1.0 and M_i =-1.0 directly correspond to post-manipulation changes in Y +1.0 and -1.0 mg L^{-1}, respectively. Time series of predicted upstream-downstream differences (Y_{pred}) were calculated for each solute form using the null model and the best model (if different).

The coefficient of variation (*CV*) of *Y* was calculated for pre- and post-manipulation phases for each solute form, which on the basis of hydraulics only, would be expected to increase; stated another way, with a decrease in water residence time, the "load dampening potential" of the ecosystem should also decrease. We examined evidence for coupled cycling of solute pairs (e.g., $Y_{sulfate}$ and $Y_{nitrate}$), grouped by pre- and post-manipulation phases, using ANCOVA.

2.5 Hydrology and Estimation of Instantaneous Net Solute Fluxes

Time series of instantaneous net solute fluxes across the manipulated reach were used to evaluate dynamics of the Big Spring ecosystem. Along with solute concentration measurements, discharge (Q) was measured at both input and output stations (same as reference and treatment stations in the autoregressive analysis) using a velocity×area technique for calculation of loads ($C\times Q$). Solute mass outputs (O) were estimated as the product of discharge and solute concentration at the stream output station ($Q_O\times C_O$). Total solute mass inputs (I_{TOT}) were estimated from the sum of three input stations ($I_{\mathrm{TOT}}=I+T+G$) where I is mass input from the primary input station ($Q_I\times C_I$) which constituted the majority of loading, T is mass input from one minor surface water tributary within the study reach (Buckley Creek, with discharge term Q_T), and G is mass input from groundwater (with discharge term Q_G). Q_T and Q_G required for calculation of T and G were estimated from

$$Q_T = b\times Q_I \qquad \text{(Eq. 4)}$$

$$Q_O = Q_I + Q_T + Q_G - Q_S - Q_E \qquad \text{(Eq. 5)}$$

where b is an empirically-determined coefficient driven by hydrologic coherence of the two tributaries (mean b =0.14; 1 s.d.= 0.03; n=9), and Eq. 5 is the water balance with Q_S as seepage (into groundwater) and Q_E as evapotranspiration. Given consistent hydrologic gains over the study reach (Q_O ~1.25× [$Q_I + Q_T$]), and a low stream gradient (0.15 %), we assumed Q_S=0. We also assumed $Q_E = 0$. T was estimated as T=Q_T(t) × $\overline{C}_T$, where $\overline{C}_T$ = mean C_T. G was estimated as $G = Q_G$(t) × $\overline{C}_G$, where $\overline{C}_G$ is mean C_G. Water samples from a surface spring near the primary region of groundwater discharge (lower end of study reach) were used to represent C_G. This spring was sampled at a lower frequency than C_I and C_O under the expectation of a relatively static groundwater solute pool, and there were no significant linear trends for C_T or C_G within or among years. Observed spring chloride (C_G) was compared to expected spring chloride under conservative transport (E= [O -I-T] / Q_G) to evaluate the assumption that spring water was representative of groundwater chemistry.

Net solute flux was calculated as a percentage of inputs (F_{net}=100×[O/I_{TOT} -1]). Predicted net solute fluxes were calculated from the null model and best model of each solute form (if different) by replacing O in the immediately previous equation with the predicted solute outputs (O_{pred}=[Y_{pred}+C_I]×Q_O). Because these predicted solute fluxes are based on simple models, they are representative of aggregate trends but do not always capture individual outliers/extremes.

2.6 Hydrogeomorphology

Supporting hydrogeomorphic measures were determined pre- and post-manipulation using 6 experimental (pulse) releases of conservative tracer [*Stream Solute Workshop*, 1990]. We used either chloride or bromide in solute releases, and estimated conservative parameters using high frequency solute time series estimated from solute ~specific conductivity relationships in a transient storage model [*Gooseff and McGlynn*, 2005]. See Powers et al. [2009] or Payn et al. [2008] for field and modeling approaches involving pulse solute releases. Mean water velocity ($u = \overline{Q}/A$, where $\overline{Q} = (Q_I + Q_O)/2$), and mean water residence time ($\tau = L/u$, where $L = 1.4$ km) were estimated for pre- and post-manipulation phases.

2.7 Laboratory Methods

Several solute forms were measured. Nitrate (operationally, nitrate + nitrite; NO_3-N), ammonium (NH_4-N), total dissolved N (TDN), and total dissolved phosphorus (TDP) were determined by flow-injection analysis on an Astoria Pacific Instruments autoanalyzer (APIA). Chloride (Cl^-) and sulfate (SO_4^{2-}) were determined by ion chromatography on a Dionex DX-500. Soluble reactive P (SRP) was determined colorometrically using the molybdate blue method [APHA 1995] and a Beckman spectrophotometer. DON and DOP were estimated by difference (DON=TDN-DIN, where DIN=nitrate + nitrite + ammonium; DOP=TDP-SRP).

Additional variables were measured for site characterization only. Total suspended sediment (TSS) and percent organic matter in suspended sediment (OM) were measured by standard methods. Water temperature was logged at output and main input stations. Dissolved oxygen and pH were measured near the beginning of the study.

3. Results

3.1 Hydrology, Hydraulics, and Channel Form

Groundwater discharge (Q_G) of the study reach was always positive (range from 14 to 30 % of mainstem input discharge (Q_O), or a gain of 25-40% over the study reach; Table 3), indicating a persistent net gain. Hydrogeomorphology of the study reach was altered incrementally in 2008 by the management manipulation (Fig. 2). Ultimately, between July 2008 and September 2008, mean wetted width (w) decreased from 20.0 to 8.0 m and mean water travel time (τ) decreased from 4.0 to 1.5 hrs (mean velocity increase from 0.097 to 0.26 m s^{-1}). This was also associated with short-term erosion of sediment and organic matter from the study reach, which abated following 2008. Mean observed chloride concentration of spring water (± 1 s.d) was 1.7 ± 0.16 mg L^{-1} (n=12) and similar to expected spring chloride concentration under conservative transport (E=1.9 ± 1.1 mg L^{-1}). The considerable deviation for E is largely attributable to error propagation from the multiple terms required to estimate this value.

3.2 Pre-manipulation Solute Transport

Mainstem surface water input (I) represented the majority of total input (I_{TOT}) for all solute forms, except in the case of DON. Mean instantaneous solute fluxes are reported in Table 4. On average, chloride transport was approximately conservative prior to manipulation (mean F_{net} = -1.1 ± 4.4, n=19; Fig. 3) with variability that is most likely within the bounds of discharge and analytical errors. Sulfate was consistently retained within the study reach (mean F_{net} = -3.9 ± 2.3; Fig. 4) with no observations of F_{net} >0.0. Other solute forms were seasonally-variable. There was a net sink for nitrate during the warm season (F_{net} = -4.4 ± 6.9). The magnitude of instantaneous nitrate retention was often larger (F_{net} < -10.0 in 7 instances). Warm season average F_{net} values for other solute forms were as follows: ammonium, -33.6 ± 42.1; soluble reactive P, -3.4 ± 32.7; dissolved organic N, 27.7 ±161.0; dissolved organic P, 21.6 ± 107.4. There was a significant negative relationship between the upstream-downstream difference in sulfate ($Y_{sulfate}$) and the upstream-downstream difference in nitrate ($Y_{nitrate}$; Fig. 5; slope= -0.74 ± 0.17 s.e., p=0.001, adjusted r^2= 0.30). No other solute pair had any significant relationship during either the pre-manipulation phase.

3.3 Post-manipulation Solute Transport

Parameter estimates from best models of upstream downstream differences ($Y = C_O - C_I$) are reported in Table 5. For chloride, there were no significant changes in Y associated with the management manipulation. On average, chloride was transported approximately conservatively following manipulation (mean F_{net} = 1.6 ± 5.9).

For every solute form other than chloride, there was either a significant increase in Y, or a lower CV for Y, following manipulation. Y increased in the cases of ammonium, nitrate, and sulfate. For both sulfate and nitrate, the simple effect model had the lowest AIC_c, but was separated by only 1.9 AIC_c units from one other model (annual effect model in the case of nitrate, seasonal effect model in the case of sulfate); both models nonetheless yielded similar predictions for the post-manipulation phase (increase in Y). The best model for ammonium was the annual effect model, with higher Y occurring in the first year following dam removal (B_4=0.021 mg L^{-1}) compared to the second year (B_5=0.0054 mg L^{-1}). The magnitude of increase for Y was sufficient to shift the mean warm season flux of ammonium from a net sink to a net source (shift in F_{net}

from -0.30 to 49.0). Instantaneous net flux for sulfate shifted toward conservative transport (mean F_{net} = 0.1), which due to variability post-manipulation resulted in both slightly positive and slightly negative values for instantaneous net flux. Mean warm season flux for nitrate shifted from a net sink (F_{net} = -2.0) to a net source (F_{net} = 5.0) following manipulation, resulting in a substantial change in N-loading downstream of the study reach. Post-manipulation, there were no instances in which net retention of nitrate exceeded 10% of inputs.

Solute concentration changes in relation to manipulation were not detected for models of SRP, DON, or DOP. For SRP, however, the range and CV of Y were both smaller post-manipulation (range from -0.34 to 0.31, CV=3.5) relative to pre-manipulation (range from -0.61 to 0.77, CV=14.4). Ranges and CV's for DON and DOP were also lower following manipulation, which primarily reflects the disappearance of higher values and potentially, loss of transient DON and DOP sources within the study reach. Model coefficients reported in Table 5 were significant at the α=0.05 level, except for SRP (no significant coefficients), M_{year2} in the cases of ammonium (p=0.067), and B_0 in the cases of DON and DOP. In contrast to the pre-manipulation phase, when there was a linear relationship between $Y_{sulfate}$ and $Y_{nitrate}$, no solute pair had any significant relationship post-manipulation.

4. Discussion

Small impoundments are abundant within agricultural river networks, and in aggregate may be influential to downstream deliveries of fertilizing nutrients and toxins. Mature impoundments such as the former Big Spring reservoir-wetland also foreshadow the trajectory for numerous aging and neglected dams, whose biogeochemical role will likely shift with ongoing sedimentation, management intervention, or infrastructure decline/failure. Ultimately, impoundment succession could serve as a widespread mechanism of wetland creation, but this depends on management decisions involving aging infrastructure. Research is needed to better understand the biogeochemical role of reservoir-wetlands, which could be distinct from other water body types.

Prior to manipulation, the biogeochemical role of the Big Spring reservoir-wetland was influenced by >100 years of accumulated agricultural sediment and organic matter behind a small dam, shallow water column depth, a stable flow regime, and an open canopy. These features were associated with prolific benthic algae and macrophytes during the warm season [*Julian, et al.*, 2010]. In turn, the annual periodicity of solute retention for nitrate and ammonium, and possibly also SRP, prior to manipulation clearly coincided with seasonal cycles of algal growth and senescence within the study reach. Sulfate retention, however, was more persistent throughout the year. Fine reservoir sediments possessed the distinct sulfide odor, which suggests this modest level of sulfate retention may be attributable to sulfate-reducing bacteria, leading to production of hydrogen sulfide. For DON and DOP, concentrations were low relative to other systems such as peat-rich wetlands, and also net fluxes were more variable (as a fraction of inputs) than other solute forms, but the reservoir-wetland was a net source for these organic solutes during most days of observation. This is consistent with conventional thinking about wetlands as sources of dissolved organic matter to downstream ecosystems [*Mulholland*, 2003]. In contrast, F_{net} for chloride trended toward 0.0, consistent with the conservative transport expectation for this solute. Note that in a small number of instances, chloride net flux exceeded

10% of *I*, which is probably outside the bounds of discharge observation errors and could indicate modest misrepresentation of inputs for chloride or other solutes.

In addition to simple algal uptake of nutrients, there was evidence of coupled biogeochemical processes within the reservoir-wetland. Recent studies have emphasized a linkage between N and S cycling in aquatic ecosystems [*Burgin and Hamilton*, 2008; *Whitmire and Hamilton*, 2005] and we saw evidence of this (negative relationship between $Y_{sulfate}$ and $Y_{nitrate}$ prior to manipulation, each a relative measure of net flux, in Fig. 5). Our reported negative relationship between $Y_{sulfate}$ and $Y_{nitrate}$ is consistent with the suggestion of *Burgin and Hamilton* [2008] that chemolithoautotrophic bacterial metabolism of excess nitrate in stimulates sulfate production. Two associated hypotheses include: a) linkages between N and S cycling are stronger in wetlands relative to streams (or absent in streams); b) benthic disturbance severs the aquatic N-S linkage (for example, through co-release of nitrate and sulfate, which occurred in the period shortly after manipulation in 2008). Similarly, while the relationship between $Y_{ammonium}$ and $Y_{nitrate}$ was not statistically significant pre- or post-manipulation, others have reported coupling between nitrification and denitrification in aquatic systems [*Seitzinger, et al.*, 2006], and this aides interpretation of our results. Prior to manipulation, reservoir sediments were likely ammonium-rich (note the release of ammonium upon manipulation). The presence of a substantial benthic ammonium pool combined with detectable net ammonium retention points to a potentially active population of nitrifying bacteria, which would in turn generate a novel (biological) input of nitrate from within the study reach. If true, the near-balance of measured nitrate inputs and outputs during the reservoir-wetland state over the annual scale ($O=0.98*I$, Table 4) should actually be interpreted as reasonable evidence of aquatic denitrification

[*Deemer, et al.*, 2011; *O'Brien, et al.*, 2011] because algal uptake alone does not explain long-term retention of nitrate. Coupling between nitrification and denitrification also provides a reasonable explanation for an apparent lag in the seasonal peak for net nitrate retention (plotted minima in Fig. 4) behind that of ammonium, which was most evident in the year 2006.

After manipulation, channel narrowing and increased water velocity were evident from both visual observations and measurements, ultimately producing a stream state. Seasonal net sinks for nitrate and ammonium within the reservoir-wetland were in turn reduced by a shift toward export, most easily discerned from the higher warm season values in Fig. 4 following manipulation. An annual net sink for sulfate was also eliminated. Models did not detect statistical changes in mean DON or DOP, but the lower CV following manipulation suggests that the propensity for releases of organic solute may have been reduced. It is also important to recognize that our simple models are appropriate for detecting large changes in aggregate biogeochemical functionality, but are generally poor predictors of certain process details such as the range (maxima/minima) of net retention. A new trajectory of ecosystem succession continues to unfold at Big Spring Creek.

We have focused our effort on quantifying the net biogeochemical role of a small impoundment, and examining changes in that role following an experimental manipulation which caused channelization and wetland loss. But why should solute fluxes change in response to the manipulation? The change in flowpath hydraulics (water residence time) provides, at minimum, a partial explanation. At the ecosystem level, possible responses of net solute flux to a decrease in water residence time, *ceteris paribus*, include: a) reduced absolute value of mean flux (shift in magnitude toward zero, but conserved sign); b) reduced temporal variability of instantaneous flux, even if the mean remains unchanged (increased similarity of input and output time series). While many other factors could potentially explain altered solute fluxes in relation to the manipulation, we prefer the hydraulic explanation on the basis of its consistency; either the magnitude or variability of net solute fluxes was reduced for every measured solute form except chloride. Because bathymetry and morphometry are closely related to hydraulics, this may offer a convenient basis for predicting individual or aggregate (basin-level) impoundment functioning as impoundment structure changes with age, intervention, or new dam construction.

Nonetheless, some aspects of biogeochemical change following manipulation are not explainable from hydraulics alone. These "non-hydraulic" processes include: mobilization of pre-existing solute pools associated with sediments, particulate organic matter, or porewaters; creation or elimination of pre-existing gross sources or gross sinks of solute; alteration of hydrologic connections which can shift the relative influence of solute sources or sinks. In particular, reservoir drawdown can promote rapid release of ammonium from newly exposed sediments [*Perrin, et al.*, 2000]. This probably explains why some of the highest observations of ammonium concentration in our study occurred at the output sampling station during the initial phase of manipulation (prior to major changes in hydrogeomorphology). There is also statistical support for such mobilization of ammonium, due to selection of the annual effect model which is not explainable on the basis of hydraulic changes alone. Biogeochemical functioning of the study reach is best interpreted with knowledge of the full chronology of impoundment succession. This chronology, including both rapid transitions (→) and slow transitions (→→), proceeds as follows: 1- natural/historic stream → 2- young impoundment →→ 3- mature impoundment → 4-

young restored stream →→ 5- mature restored stream. Our study captured a subset of this chronology (3- mature impoundment → 4- young restored stream). Meanwhile, the final state (5- mature restored stream condition) has not yet been achieved, and could be years away due to legacy effects of impoundment and ongoing reconfiguration of channel morphology. For example, drying of exposed aquatic sediments can promote mineralization of organic matter [*Qiu and McComb*, 1996], while re-wetting can promote release of leachate, so remnant reservoir sediments along restored channel banks (visible in Fig. 2) may persist as a low-level source of solute (relative to other inputs) for years. Thus, it is important to recognize that each phase impoundment succession is structurally and functionally different, yet interdependent due to legacy effects or “memory” of previous states.

Within the US, numerous small dams are coming of age but lack coordinated management [*Doyle and Havlick*, 2009], and history provides a warning on this subject. Abandonment and breaching of tens of thousands of small mill dams in the northeastern US during the 17th to 19th centuries resulted in major wetland losses, channel alterations that are resistant to restoration, and legacy sources of fluvial sediment [*Hamilton*, 2011; *Schenk and Hupp*, 2009; *Walter and Merritts*, 2008]. In the next few decades –barring intervention– some impoundments will have substantially shallower depth and altered morphometry due to particle sedimentation. Reservoir sedimentation could in turn feedback either positively or negatively on regional surface water quality, or perhaps greenhouse gas emissions, although our current ability to predict these outcomes is hindered by a lack of information about small impoundment functioning. Regardless, impoundment density continues to increase in many nations, especially within regions of expanding agricultural extent. For example, in the US, the total surface area of small freshwater ponds increased more than 11% between 1998 and 2004 [*Dahl*, 2006]. During the early 2000's, impoundment density was also increasing at 1-2% per year in agricultural areas of the US and 60% per year in dry agricultural regions of India [*Downing, et al.*, 2006]. These widespread alterations to the routing of polluted continental water are major concerns for the management of dams and surface water pollution.

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Table 1. Baseflow physicochemistry and hydrology of the Big Spring Creek study reach during the warm season (May 15-Sep 15, 2005-2010). Physicochemistry is from the main input (*I*) station.

Category	Variable	Range
Physicochemistry	Nitrate-N (mg L^{-1})	2 - 3
	Ammonium-N (mg L^{-1})	0 - 0.05
	Total dissolved N (mg L^{-1})	2 - 3
	Total N (mg L^{-1})	2 - 3
	Dissolved organic N (mg L^{-1})	0 - 0.25
	Soluble reactive P (mg L^{-1})	0 - 0.04
	Total dissolved P (mg L^{-1})	0.01 - 0.05
	Total P (mg L^{-1})	0.02 - 0.1
	Dissolved organic P (mg L^{-1})	0.00 - 0.01
	Chloride (mg L-1)	1 - 1.5
	Dissolved organic carbon (mg L^{-1})	2 - 3
	Sulfate (mg L^{-1})	7 - 9
	DIN:SRP (atomic ratio)	30 - 50
	pH	7.5 - 8.0
	Water temperature	12 - 18
	Dissolved oxygen (mg L-1)	8 - 12
	Dissolved oxygen, % saturation	80 - 100
	Total suspended sediment (mg L^{-1})	1 - 4
	Organic matter in suspended sediment (%)	10 - 30
Hydrology	Inflow discharge (Q_I, $m^3\ s^{-1}$)	0.18 - 0.25
	Outflow discharge (Q_O, $m^3\ s^{-1}$)	0.28 - 0.45
	% Discharge gain	25 - 40

Table 2. Candidate models of post-manipulation change in solute transport through the Big Spring study reach following loss of the reservoir wetland. The response variable for all models is $Y = C_O - C_I$, where C_O is the time series of solute concentration at the output station, and C_I is the time series of solute concentration at the main input station.

Candidate model	Parameters	*k*
null (no effect of manipulation)	B_0	1
simple effect	B_0, M_{simple}	2
seasonal effect	B_0, M_{warm}, M_{cool}	3
annual effect	$B_0, M_{year1}, M_{year2}$	3

Table 3. Hydrologic terms for the Big Spring Creek study reach. Values are means, with ranges in parentheses. Q_O is mainstem stream output (n=56), Q_I is mainstem stream input, Q_T is tributary input, and Q_G is groundwater input.

	Q_O (Output	Q components, % of Q_O		
Phase	discharge, $m^3 s^{-1}$)	Q_I	Q_T	Q_G
pre	0.39 (0.31-0.49)	68 (54-79)	11 (7.4-16)	21 (14-30)
post	0.39 (0.35-0.44)	72 (53-79)	9.7 (7.3-16)	18 (14-30)

Table 4. Mean inputs and outputs of solute for the Big Spring Creek study reach. Flux components are expressed as a percentage of total inputs (I_{TOT}). I is % mainstem stream input, T is % tributary stream input, G is % groundwater input, and O is % mainstem output. O_{summer} is % mainstem output for the warm season only (May 15 and September 15).

			I_{TOT} (Total Input Mass, kg d^{-1})	Flux components, % of I_{TOT}				
Solute Category	Solute Form	Phase		I	T	G	O	O_{summer}
Inorganic solute	Cl^-	pre	99	71	17	12	99	99
	Cl^-	post	103	76	14	10	102	102
	NH_4-N	pre	1	56	35	9	71	66
	NH_4-N	post	1	74	21	6	149	160
	NO_3-N	pre	77	79	10	11	98	95
	NO_3-N	post	83	83	8	9	105	103
	SO_4^{2-}	pre	282	66	15	19	96	96
	SO_4^{2-}	post	278	70	13	17	100	99
	SRP	pre	1	65	9	26	97	97
	SRP	post	1	72	7	21	105	111
Organic solute	DON	pre	3	43	46	11	131	128
	DON	post	2	24	61	14	63	94
	DOP	pre	0	51	49	0	118	122
	DOP	post	0	55	45	0	91	88

Table 5. Best models of solute concentration during the Big Spring Creek management manipulation. Time series of the upstream-downstream difference in solute concentration ($Y=C_O-C_I$) were evaluated for a change in response to manipulation. Four different models were compared: 1) no change pre- vs. post-manipulation (intercept parameter B_0 only); 2) simple one-step change (B_0, plus parameter M_{simple} for changes incurred following manipulation); 3) season-specific change (B_0, plus parameter M_{warm} for changes incurred during the warm season, and M_{cool} for changes incur incurred during other post-manipulation seasons); 4) year-specific change (B_0, plus parameter M_{year1} for changes incurred in the first year following manipulation, and M_{year2} for changes incurred thereafter).

Solute Form	Best Model	Parameter Estimate (± 1 standard error)	Δ*AICc* (Improvement over "no change" model)	*k* (best model)
Cl^-	null	B_0= -0.18 ± 0.029	-	1
DON	null	B_0= 0.0045 ± 0.0092	-	1
DOP	null	B_0= 0.00030 ± 0.00037	-	1
SO_4^{2-}	simple effect	B_0= -0.14 ± 0.064, M_{simple} = 0.22 ± 0.091	4.8	2
SO_4^{2-}	annual effect	B_0= -0.14 ± 0.059, M_{year1} = 0.35 ± 0.11, M_{year2}= 0.12 ± 0.099	6.7	3
NO_3-N	simple effect	B_0= -0.41 ± 0.022, M_{simple} = 0.11 ± 0.033	12.1	2
NO_3-N	annual effect	B_0= -0.41 ± 0.022, M_{year1}= 0.13 ± 0.043, M_{year2}= 0.097 ± 0.039	10.4	3
NH_4-N	annual effect	B_0= -0.0020 ± 0.0016, M_{year1}= 0.021 ± 0.0034, M_{year2}= 0.0054 ± 0.0029	23.0	3
SRP	seasonal effect	B_0= -0.00019 ± 0.00077, M_{warm}= 0.0019 ± 0.0014, M_{cool} = -0.0023 ± 0.0014	2.7	3

Figure Legends

Figure 1. Big Spring Creek prior to manipulation, and surrounding catchment. The study reach is bounded by the dashed box. Flow direction is left to right. Key: dark gray= wetlands or ponds; black lines= streams; cross= dam site; leftmost circle= main input sampling station (*I*); rightmost circle= output sampling station (*O*); square= tributary (Buckley Creek) sampling station (*T*); up-turned triangle = groundwater sampling station (*G*); down-turned triangle= large headwater spring; white= agricultural land (cultivated and pasture); light gray= grassland/shrub; medium gray= mixed forest.

Figure 2. The Big Spring Creek study reach, pre- manipulation (reservoir-wetland state) and post-manipulation. Photos are from July 2008 (immediately prior to initial dewatering), and July 2010. Mean wetted width (*w*) of the study reach decreased from 20 m to 8.0 m.

Figure 3. Instantaneous net fluxes of chloride and organic solute through the Big Spring study reach. Modeling did not detect pre-post changes in the upstream-downstream difference in concentration (Y=C_O-C_I) for these solutes. Fluxes are reported as the percent of daily inputs. Black dots are pre-manipulation. White dots are post-manipulation. Dots above/below the conservative transport expectation (0.0, gray line) indicate net export/retention. Solid lines are flux predictions from the best model (no change). Modeling suggested a change following manipulation for net solute flux of SO_4^{2-}, NO_3-N, and NH_4-N.

Figure 4. Instantaneous net fluxes of sulfate, nitrate, ammonium, and soluble reactive phosphorus through the Big Spring study reach. Modeling detected pre-post changes in the upstream-downstream difference in concentration (Y=C_O-C_I) for these

solutes. Black dots are pre-manipulation (reservoir-wetland state). White dots are post-manipulation. Dots above/below the conservative transport expectation (0.0, gray line) indicate net export/retention. Solid lines are flux predictions from the best model. Dashed lines are predictions from the no change model.

Figure 5. Change in the relationship between sulfate and nitrate following manipulation. Axes are plotted as the difference between output concentration and main input concentration ($Y=C_O-C_I$). Black dots are pre-manipulation (reservoir-wetland state). White dots are post-manipulation. Black line is linear regression of pre-manipulation data (slope= -1.61 ± 0.44 s.e., p=0.001, adjusted r^2=0.31; intercept= -0.81 ± 0.19 s.e., p= 0.0002).

Figure 1.

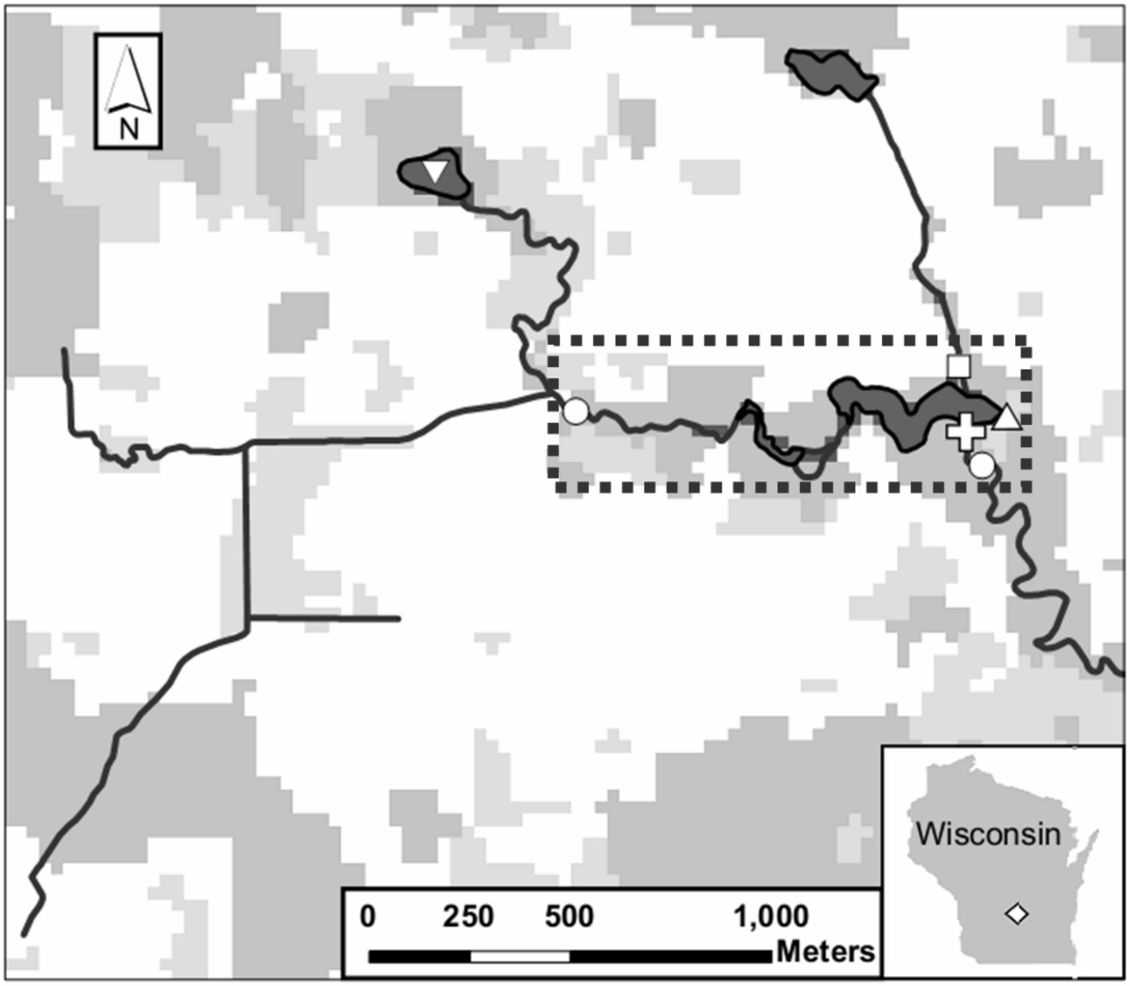


Figure 2.

Figure 3.

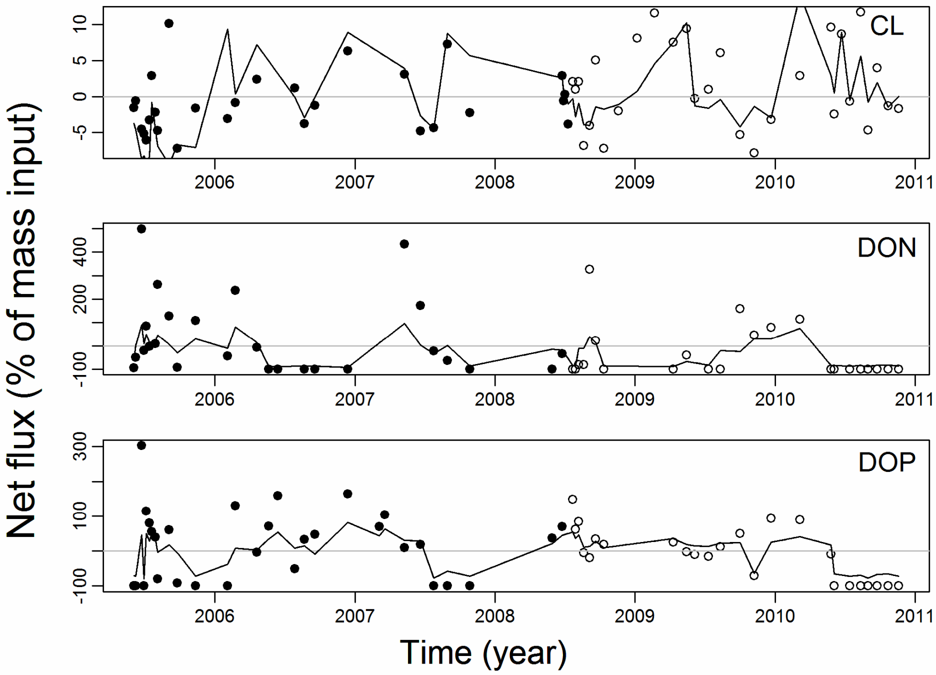
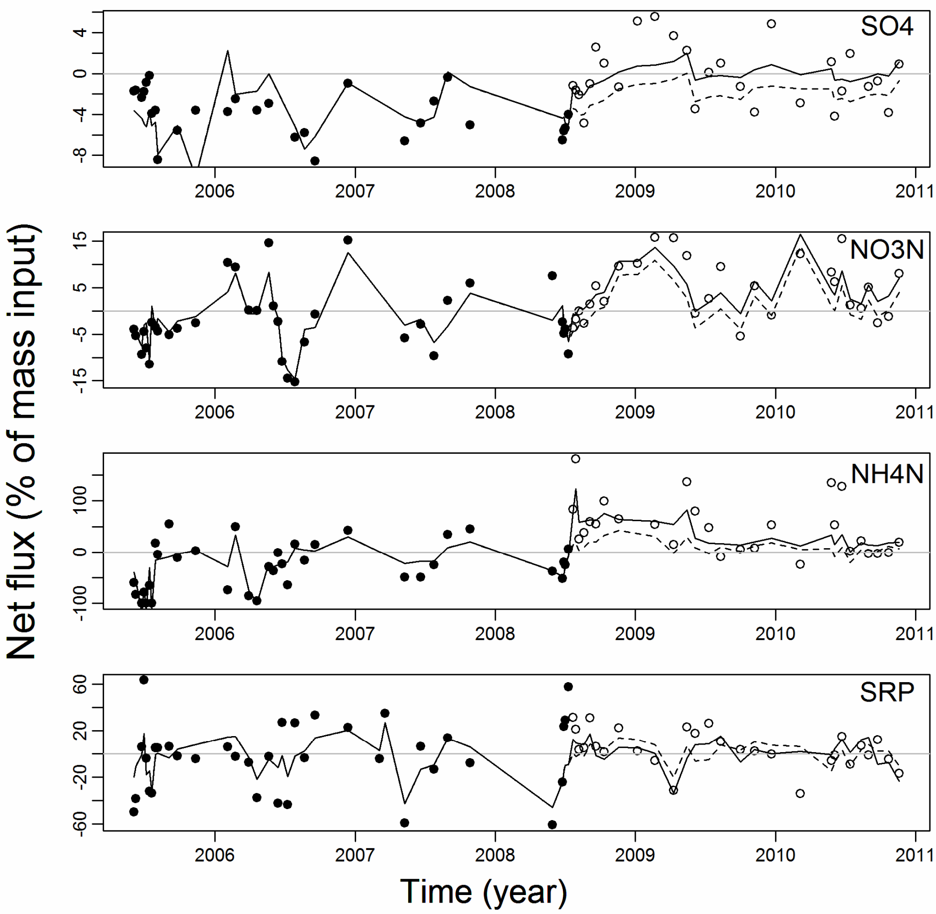

Net flux (% of mass input)
Time (year)
CL
DON
DOP
10
5
0
-5
400
200
-100
300
100
-100
2006
2007
2008
2009
2010
2011

Figure 4.


SO4
NO3N
NH4N
SRP
4
0
-4
-8
15
5
-5
-15
100
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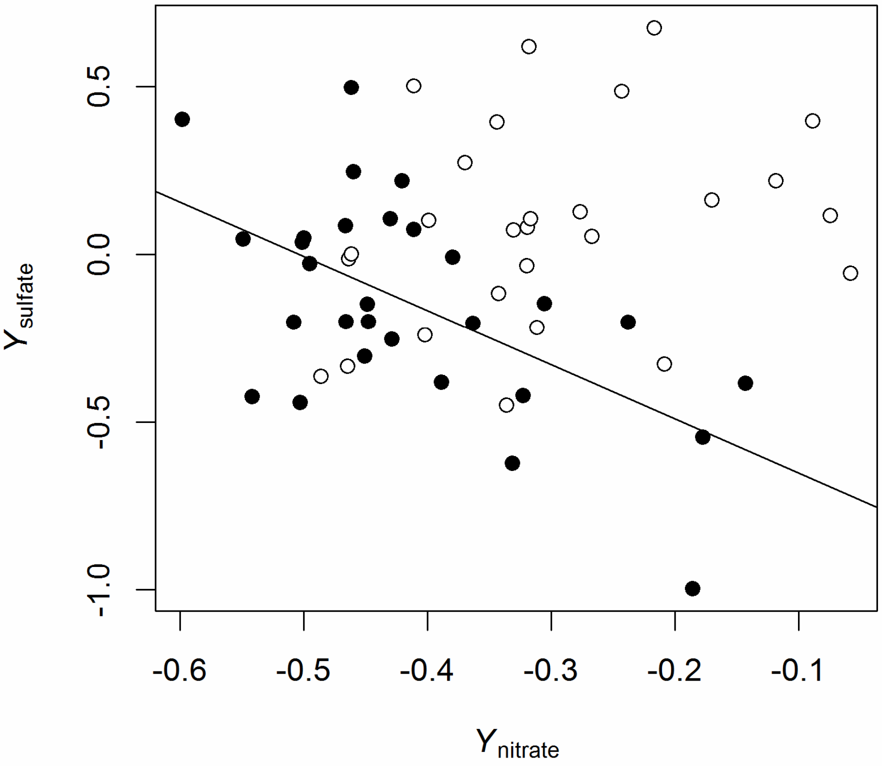
20
-20
-60
2006
2007
2008
2009
2010
2011
Net flux (% of mass input)
Time (year)

Figure 5.



Appendix B. Expanded methods for solute time series modeling

We tested for changes in solute concentration due to manipulation using intervention analysis [*Box and Tiao*, 1975] and autoregressive time series modeling. Our goal was to evaluate simple alternative responses of solute to manipulation while conserving. Modeling was conducted independently for each solute form. A detailed modeling example using the nitrate data is provided below.

In the case of nitrate, autocorrelation for Y was evident in preliminary analysis, indicating the likely need for an autoregressive model structure. More specifically, the Durbin-Watson test indicated statistically significant spikes in the autocorrelation function (ACF) and partial autocorrelation function (PACF) at lag1, but not at higher lags (Figure A). Lag1 autocorrelation of nitrate Y may be alternatively observed in the slightly positive slope in the scatter plot of Y_{t-1} and Y_t. We postulated that Eq. 2 might provide a stationary model structure, which if true should yield: 1) an unbiased, normal distribution of model residuals; 2) a time series of residuals that is not autocorrelated. Figure B shows that equation 2 (simple effect model) does indeed yield approximately normal residuals. Figure C shows the associated time series of residuals is also not autocorrelated. Diagnostic plots for other candidate models of nitrate Y (null model, seasonal effect, annual effect) also lacked residual patterns.

Note that lack of autocorrelation at higher lags is partly influenced by irregular sampling intervals for Y, which under regular (even) sampling intervals might have yielded autocorrelation at higher lags (due to cyclical/inter-annual patterns in the data). In an attempt to address these issues, we also considered two additional models. The first was a cyclic-seasonal model, which was incompatible with the data due insufficient sample size and uneven sampling interval. The second had an alternate correlation structure to Eq. 2 that can be applicable to irregularly sampled time series, given by

$$Y = B_0 + f(d, n) + \sum_{i}^{n} M_i D_i + e_t \qquad \text{(Eq. 6)}$$

where *d* and *n* are the range and nugget parameters of an exponential correlation model fitted from the data (*Y~t*). Best models (by AIC) and associated effect sizes from this modeling approach were highly similar to that of Eq. 2. We conclude that Eq. 2, with a lag 1 autoregressive structure, is statistically robust, and enables the evaluation of simple alternative responses of solute to manipulation.

References (Appendix B)

Box, G. E. P., and G. C. Tiao (1975), Intervention analysis with applications to economic and environmental problems, *Journal of the American Statistical Association*, *70*, 70-79.

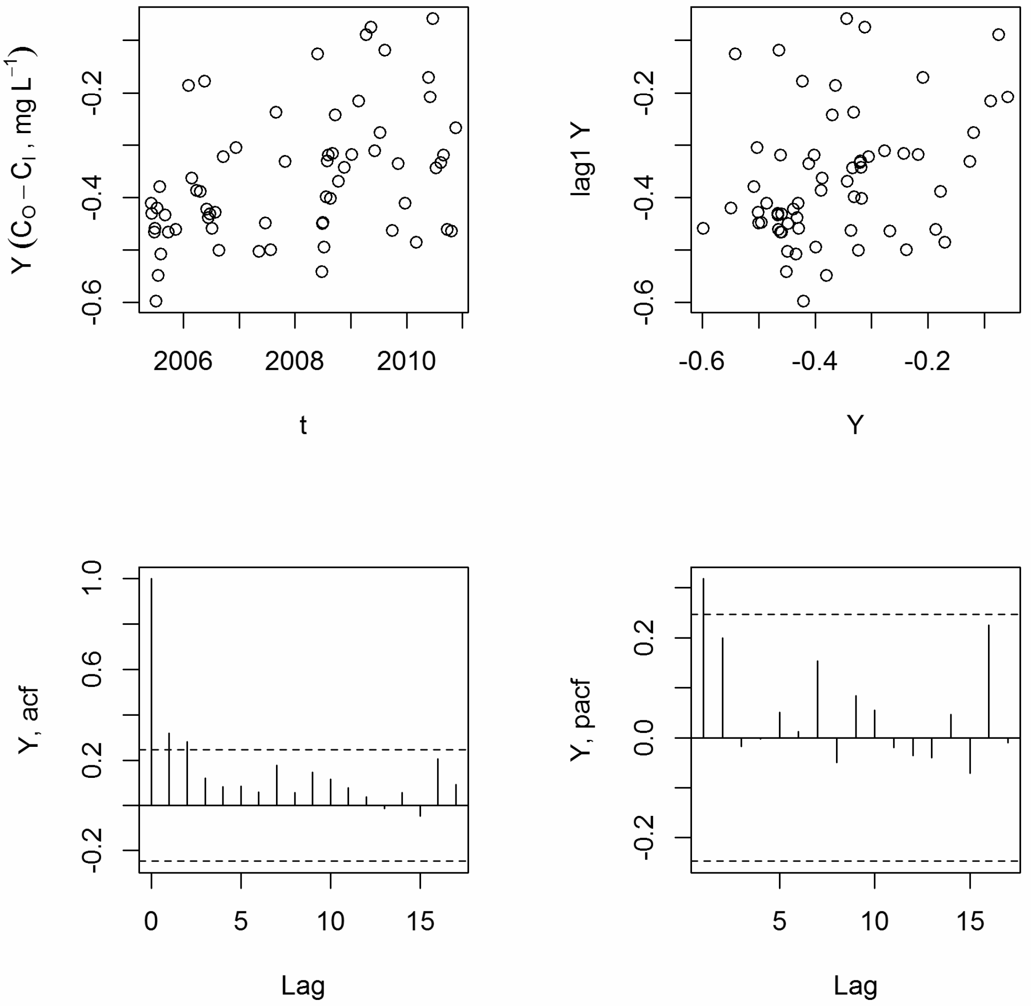


Figure A. Diagnostic plots for the intervention analysis response variable ($Y = C_O - C_I$) for one solute form (nitrate). Autocorrelation at lag1 is apparent. Bars outside of dashed lines in acf/pacf plots are significant.

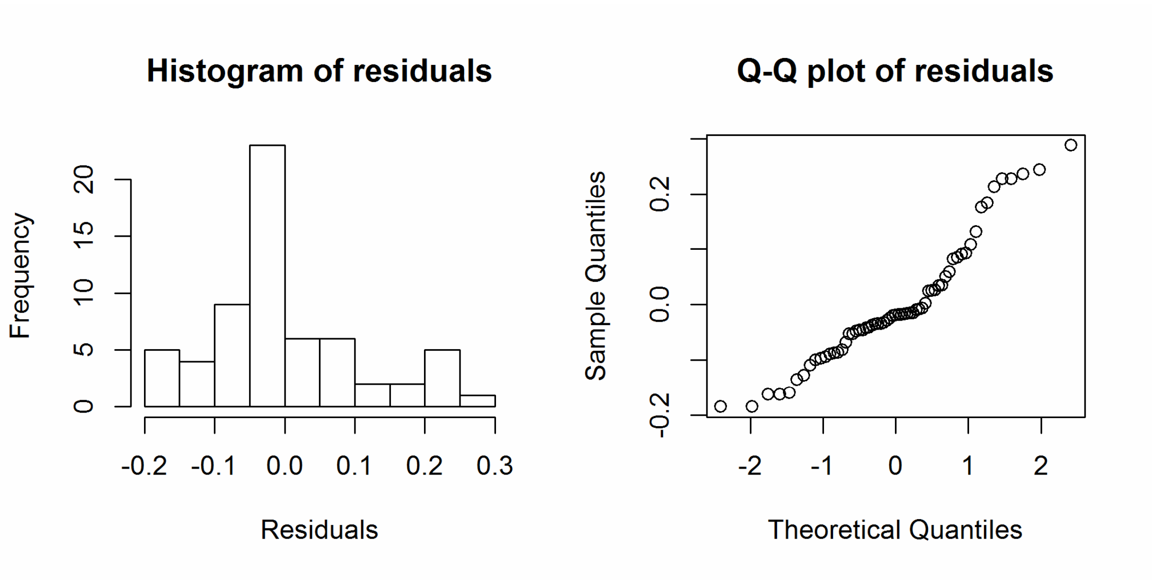


Figure B. Histogram and Q-Q plot of model residuals for one solute form (nitrate), indicating the distribution is approximately normal.

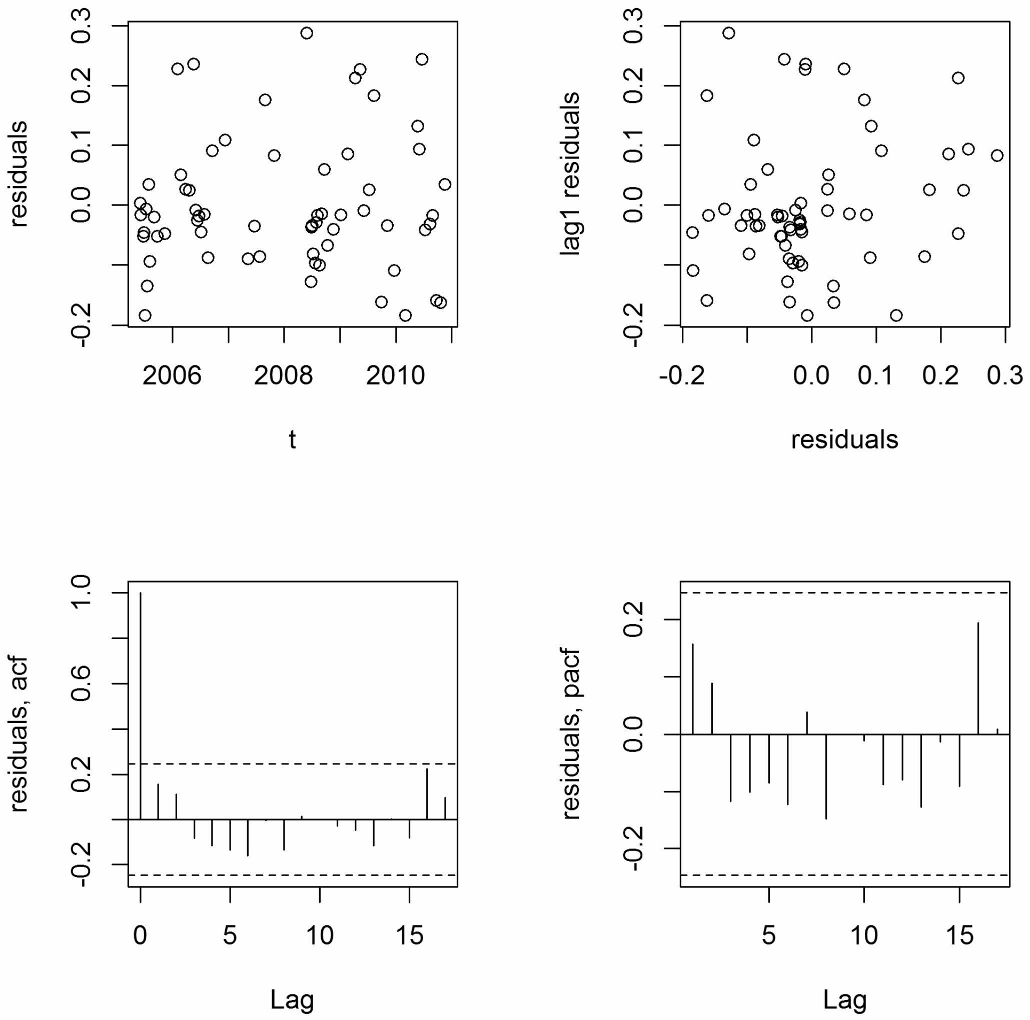


Figure C. Diagnostic plots for intervention analysis model residuals for one solute form (nitrate). The residuals are not significantly autocorrelated, suggesting model stationarity. Bars outside of dashed lines in acf/pacf plots are significant.

CHAPTER 4

AGRICULTURAL AND AQUATIC CONTRIBUTIONS TO INTER-ANNUAL VARIABILITY OF RIVER EXPORT

Abstract

Water and mass exports from rivers are influenced by processes occurring in both terrestrial and aquatic ecosystems. In particular, sources and sinks for nutrients in lentic ecosystems may be important at time scales greater than one year. We examined long-term records of annual river export (yield, and flow-weighted concentration) for total phosphorus (TP), total nitrogen (TN), total suspended sediments (TSS) using catchments in Wisconsin, USA (n=63) which varied in terrestrial composition (forested, agricultural, mixed) and aquatic composition (stream-dominated, or lotic; lake- dominated, or lentic). Across river constituent forms, there was a higher median and CV for long-term yield and flow-weighted concentration in agricultural and mixed catchments relative to forested catchments. There was also a general pattern of decrease for the median and CV of yield and flow-weighted concentration in lentic relative to lotic catchments, even in the presence of high agriculture. Differences in mass export CV's among catchments were only partly explained from water yield variability. Our results suggest that over the long-term (decades) the collective role of agricultural land is to not only increase the central tendency of mass export, but also amplify inter-annual variability, while the collective role of lakes and reservoirs is to reduce export and dampen variability. Long-term responses in the central tendency or variability of river export will depend on interacting terrestrial, aquatic, and

meteorological patterns in which the presence of lentic water bodies can dilute, dampen, and introduce lags to transport.

Introduction

Rivers are intimately linked to terrestrial landscapes. Many comparative studies have demonstrated these linkages through strong relationships between terrestrial land cover characteristics- such as percent agriculture or percent wetland in the basin- and stream/river chemistry [e.g., *Dodds and Oakes*, 2008; *Gergel, et al.*, 2002; *Peterson and Urquhart*, 2006]. The nature of these terrestrial-aquatic relationships, however, is variable over the Earth's surface. Even within the same region, small catchments can demonstrate substantial contrasts in composition [*Smith, et al.*, 2005] and research is still needed to understand how this small catchment heterogeneity contributes to mass export at a broad temporal extent (>1 yr). Increasingly, it is also recognized that catchment exports are functions of both terrestrial processes and aquatic processes.

River ecologists have recognized the modifying influence of reservoirs in classic work [*Poff, et al.*, 1997; *Ward and Stanford*, 1983]. More recently, several studies have suggested large cumulative influences of lentic water bodies (lakes, reservoirs, and wetlands) on global cycles of nitrogen [*Harrison, et al.*, 2009; *Jordan, et al.*, 2011; *Wollheim, et al.*, 2008] and carbon [*Bastviken, et al.*, 2011; *Cole, et al.*, 2007; *Tranvik, et al.*, 2009]. Further, many lentic water bodies in agricultural regions such as the midwestern US are well-positioned to intercept anthropogenic nutrient deliveries. These aquatic ecosystems can function as long-term sinks for nutrients as well as sediment that in turn shift catchment export away from expectations based on the terrestrial environment alone. Lentic ecosystems might also be expected to reduce the variability of catchment exports by functioning as transient sinks during above-average transport periods (such as through particulate settling or denitrification) but transient sources during other periods (through recycling of benthic organic matter). Thus, lentic water bodies should have an important influence on not only the central tendency of catchment exports, but also the variability, and it remains to be shown how these influences may vary with agricultural land use.

One problem for water quality management is that annual transport of river constituents can fluctuate dramatically, mainly in relation to precipitation [*Alexander, et al.*, 1996; *Goolsby and Battaglin*, 2001]. These large swings in river export have far-reaching ecological consequences. For example, high transport of agricultural nitrogen during unusually wet periods greatly expands the size of hypoxic zones the Gulf of Mexico [*Turner, et al.*, 2006]. During recovery from drought, reconnected flowpaths can deliver pulses of soil and groundwater nutrients accumulated during drier times [*Howarth, et al.*, 2006]. Among-year variability of environmental conditions has also been proposed as an engine for life history evolution, as in the case of models involving the timing of invertebrate diapause [*Cohen*, 1966; *Lytle*, 2001]. Thus, river exports may be generally viewed as an outcome of interacting terrestrial, aquatic, and climatic factors.

Here, we examine long-term (20 yr) records of water and mass export (total nitrogen, total phosphorus, total suspended sediments) for catchments in Wisconsin, USA that have contrasting agricultural intensity and surface water coverage. We focus on this question for a broad time horizon: How does river export respond to interacting terrestrial, aquatic, and climate influences?

Our approach centers on two categories of response to landscape and climate: central tendency (median) of mass export, and inter-annual variability (CV) of mass export. The above criteria illustrate important dimensions of the river export regime— patterns in mass delivery linked to flow regime— including sensitivity to land use practices, upstream hydrology, aquatic biology, and meteorologically anomalous events.

Methods

The Wisconsin landscape varies widely due to past glaciation and contemporary land practices. Today, its catchments span large gradients of agricultural coverage and surface water coverage (natural lakes and reservoirs), including some with moderate or high levels of both. We used this heterogeneous landscape to conduct a comparative study of catchment hydrology and biogeochemistry.

Stream sites having sufficient discharge and water quality information were used to examine long-term patterns of transport. For several years, records of daily discharge and repeatedly sampled total phosphorus (TP), total nitrogen (TN), and total suspended sediment (TSS) were collected by the US Geological Survey and the Wisconsin Department of Natural Resources at many stream and river sites throughout Wisconsin. Most of these records are available at the National Water Information System (NWIS) website and Environmental Protection Agency (EPA) storage and retrieval (STORET) website. We focused on catchments in the size range <6000 km^2 (Fig. 1) which excludes large order rivers (Wisconsin R, Fox R). Each of these sites contained a large number of TP, TN, and TSS samples (n>25) and also gauged daily discharge values for most years during water years 1986 through 2006. To maximize the number of sites available for analysis, we used some sites that did not have long-term records for all three constituents (for TP, n=63; for TN, n=45; for TSS, n=55); 45 had sufficient information for all three constituent forms. Some urbanized catchments contribute major point sources of nutrients (most notably, wastewater outflows), and these were excluded from our analysis in order to best isolate rural streams and rivers subjected to different levels of nonpoint agricultural runoff. Sites ranged in latitude from 42.51° to 46.68° N.

Catchment land cover characterization

The boundaries of the contributing catchment for each river site were delineated in Arcmap 10 with standard methods, using the National Hydrography Dataset (NHD) and 90-m National Elevation Dataset (NED). Total catchment area (A, L^2) was calculated. The National Land Cover Dataset (NLCD 2001, which occurred within the period of record) was used to calculate the proportion of catchment area occupied by agriculture (P_{AGR}), wetland (P_{WET}), forest (P_{FOR}), grass/pasture (P_{GRA}), and urban (P_{URB}) land cover classes. Differences in land cover classification between NLCD 2001 and other available years within the period of stream records (NLCD 1992, 2006) are broadly similar except near urban areas not included in our study. The Wisconsin Hydrography Database [Wisconsin DNR 2009] was used to determine the proportion of catchment occupied by reservoirs/flowages (P_{RF}), and the proportion occupied by lakes/ponds (P_{LP}). The sum of P_{RF} and P_{LP} is hereon referred to as lentic surface water (P_{WAT}), which reasonably excludes water occurring in large river channels.

Estimation of annual river mass and water exports

Metrics and notation are shown in Table 1. For each site, daily discharge values were summed over each water year *t* (Oct 1 to Sep 30) to estimate total annual water discharge (q_t, L^3) and annual water yield ($Q_t = q_t/A$, L). River constituent data were used to estimate annual loads (L_t, M) with using a Cohn-type seasonal regression model [*Cohn, et al.*, 1992] of daily discharge and periodically sampled river constituents (n~25 water samples for each ~5 year interval; see Appendix C). The annual yield ($Y_t=L_t/A$, M L^{-2}) and mean annual concentration ($C_t = L_t/q_t$, M L^{-3}) were also calculated. Site-specific records of C_t, and Q_t were linearly detrended (to the long-term median) for a minority of sites showing long-term trends, in order to best eliminate effects of management or land use change; Y_t was log-linearly detrended. The CV and median of detrended Y_t, C_t and Q_t were calculated for each site. Linear detrending reduced the magnitude of deviations from the median, and thereby causes a modest reduction of the CV.

Analysis and statistics

Contrasting catchment classes were defined based on land cover in the contributing basin. Landscape patterns were characterized using k-means clustering analysis for two land cover classes of primary interest (P_{AGR}, P_{WAT}). Catchments separated largely along a primary axis of terrestrial coverage (*LAND*) and a secondary axis of surface water coverage (*AQUA*), including the following classes: 1) high P_{AGR}, low P_{WAT}; 2) high P_{AGR}, moderate or high P_{WAT}; 3) intermediate P_{AGR}, low P_{WAT}; 4) intermediate P_{AGR}, moderate or high P_{WAT}; 5) low P_{AGR}, low P_{WAT} ; 6) low P_{AGR}, moderate or high P_{WAT}. For the *LAND* axis, we refer to classes 1 and 2 as *agricultural*, 5 and 6 as *forested*, and 3 and 4 as *mixed*. For the *AQUA* axis, we refer to catchment classes 1, 3, and 5 as *lotic*, while 2, 4, and 6 are *lentic*. Cross-correlation plots for other land cover classes are contained in Appendix C.

Differences for the central tendency of river TP, TN, and TSS, and water export among catchment classes were evaluated using the median of catchment outputs ($\tilde{Y}$, $\tilde{C}$, $\tilde{Q}$) with two-way ANOVA on $LAND \times AQUA$; $\tilde{Y}$ was log transformed in this analysis to meet the assumption of normality. Corresponding differences in the inter-annual variability of TP, TN, TSS, and water export among catchments were examined using the CV of catchment outputs (CV_Y, CV_C, CV_Q) with two-way ANOVA on $LAND \times AQUA$. Partial r^2 values were calculated in these analyses.

Results

Central tendency of river export

Water yield (Q_t) ranged substantially at most sites over the period of record. The maximum Q_t was recorded at Pecatonica River (1.16 m in 1993) and the minimum was at West Branch Rock River (0.04 m in 2003). Despite inter-annual variability of Q_t, $\tilde{Q}$ was rather consistent among sites (0.16 to 0.33 m) and there were no significant differences in $\tilde{Q}$ among catchment classes (two-way ANOVA, $AQUA \times LAND$).

Example Y_t time series are shown for contrasting catchment classes (Fig. 2). At each site, and across constituent forms, $\widetilde{Y}$ ranged substantially over the period of record (Fig. 3). The range for $\widetilde{Y}$ among catchment classes was 180 to 1800 g km^{-2} yr^{-1} for TN (mean=660), 12 to 120 for TP (mean=50), and 920 to 27000 for TSS (mean=12000). $\widetilde{C}$ ranged from 0.62 to 4.9 mg L^{-1} for TN (mean=2.2), 0.040 to 0.63 for TP (0.23), and 3.4 to 110 for TSS (mean=52). Averaging across catchment classes, the mean atomic ratio of N:P export was 29.

In contrast to $\widetilde{Q}$, differences in $\widetilde{Y}$ and $\widetilde{C}$ with *LAND* and *AQUA* were highly significant ($p<<0.001$, Table 3) except in the case of $\widetilde{C}$ for TP. In the case $\widetilde{Y}$, there were significant main effects of both *LAND* and *AQUA* across constituent forms. In the case of $\widetilde{C}$, *LAND* was significant for TN only, whereas *AQUA* was significant for TN and TSS, and marginally significant for TP. The interaction between *LAND* and *AQUA* was highly insignificant across constituent forms, except in the case of $\widetilde{Y}$ for TN ($p=0.09$)

When significant, the effect of *LAND* on $\widetilde{Y}$ or $\widetilde{C}$ was always positive (regardless of constituent form), indicating higher central tendency of export from catchments with higher P_{AGR} (*agricultural>forested, agricultural>mixed, mixed>forested*; Table 4). In contrast, the effect of *AQUA* was always negative, indicating lower central tendency in *lentic* relative to *lotic* catchments. For TN and TP, *LAND* explained a larger proportion of the variation in $\widetilde{Y}$ than *AQUA* (partial r squares as follows: for TN *LAND*=0.55, *AQUA*=0.04; for TP, *LAND*=0.35, *AQUA*=0.08). For TSS, *LAND* and *AQUA* explained equivalent amounts off variation (0.18). For $\widetilde{Y}$, the mean difference in TN between *mixed* and *forested* catchments (back-transformed) was

2.7 g km^{-2} yr^{-1}, and corresponding mean differences for TP and TSS were 4.0 and 3.0 g km^{-2} yr^{-1}. *Agricultural* catchments had significantly higher $\widetilde{Y}$ than *mixed* catchments, but in general these differences were smaller than differences between *mixed* and *forested* catchments. For $\widetilde{C}$, the mean difference in TN between *mixed* and *forested* catchments was 1.83 mg L^{-1}, and corresponding mean differences for TP and TSS were 0.20 and 62 mg L^{-1}.

Lentic catchments had significantly lower $\widetilde{Y}$ and $\widetilde{C}$ than *lotic* catchments. For $\widetilde{Y}$, the mean difference in TN between *lentic* and *lotic* catchments (back-transformed) was 1.44 g km^{-2} yr^{-1}, and corresponding mean differences for TP and TSS were 1.90 and 3.09 g km^{-2} yr^{-1}. For $\widetilde{C}$, the mean difference in TN between *lentic* and *lotic* catchments was 1.17 mg L^{-1}, and corresponding mean differences for TP and TSS were 0.27 and 71.64 mg L^{-1}.

Most river sampling stations lacked long-term trends for river constituents (Table A, Appendix C). For TP, 20 sites had significant long-term trends in $\widetilde{Y}$ (17 declines), 10 of which were <50%. For TN, 7 sites had significant long-trends in $\widetilde{Y}$ (4 declines). Only two sites had significant long-term linear trends in Q_t (Rattlesnake Creek, decline, p=0.001; Apple River, gain p=0.04).

Inter-annual variability of export

In contrast to $\widetilde{Q}$, there were significant differences in CV_Q among catchment classes (Table 5). This included significant differences in CV_Q with *LAND* and *AQUA* for TP and TSS sites, while only *LAND* was significant for TN sites (n=45, relative to 63 for TP and 55 for TSS). Across catchment classes, CV_Q ranged from 0.19 to 0.42 (mean= 0.29).

CV_Y is not often reported for long-term annual river export. The range for CV_Y among catchment classes was 0.22 to 0.42 for TN (mean=0.30), 0.21 to 0.41 for TP (mean=0.40), and 0.23 to 0.92 for TSS (mean=0.53). The range for CV_C was 0.02 to 0.11 for TN (mean=0.05), 0.04 to 0.25 for TP (mean=0.13), and 0.05 to 0.58 for TSS (mean=0.28). CV_Y: CV_Q ranged from 0.98 to 1.2 for TN, 1.1 to 1.7 for TP, and 1.0 to 2.3 for TSS. The only catchment class with CV_Y: CV_Q <1.0 was *lentic-forested* (TN), indicating lower Y_t variability relative to Q_t variability. In the case CV_Y, there were significant effects of both *LAND* and *AQUA* for all constituent forms. In the case of $\widetilde{C}$, *LAND* was significant for TN only, whereas *AQUA* was significant for all constituent forms. The interaction between *LAND* and *AQUA* was insignificant across constituent forms.

There were significant differences with *LAND* and *AQUA* for both CV_Y and CV_C. The direction of significant *LAND*/*AQUA* effects on CV_Y and CV_C was identical to those of $\widetilde{Y}$ or $\widetilde{C}$, although partial r squares were lower for the CV's. When significant, the effect of *LAND* on CV_Y or CV_C was always positive (regardless of constituent form), indicating higher variability of export from catchments with higher P_{AGR} (*agricultural>forested, agricultural>mixed, mixed>forested*; Table 4). In contrast, the effect of *AQUA* was negative for TP and TSS (not significant for TN), indicating lower variability in *lentic* relative to *lotic* catchments. For TN and TSS, *LAND* explained a larger proportion of the variation in CV_Y than *AQUA* (partial r squares as follows: for TN *LAND*=0.21, *AQUA*=0.04; for TSS, *LAND*=0.17, *AQUA*=0.10). For TP, *AQUA* explained a larger proportion of the variation in CV_Y than *LAND* (0.16>0.10). For CV_C, the only constituent form with a significant effect of *LAND* was TN (*agricultural>forested*, *agricultural>mixed*).

For TP and TSS, *lentic* catchments had significantly lower CV_Y than *lotic* catchments. For TN, the difference was significant for CV_C but not CV_Y . For TP, CV_C in *lentic* catchments was also significantly lower relative *lotic* catchments, and the corresponding comparison for TSS was marginally significant (p=0.067).

Discussion

River nutrient and sediment exports are a function of interacting terrestrial, aquatic, and meteorological influences, and could be sensitive to future changes in land use or climate. We examined records of river total nitrogen, phosphorus, and sediment, and found a strong positive influence of agriculture on not only the central tendency of long-term export, but also inter-annual variability. While the influence of aquatic composition (upstream lentic water bodies) was generally smaller than that of terrestrial composition, aquatic effects were consistent and negative. Further, the magnitude of this aquatic dampening effect on river exports, and more generally the strength of landscape influences- varied among constituent forms, with agricultural intensity in the catchment.

Terrestrial influences on river export

To date, studies relating terrestrial landscape characteristics to river water quality variables have been dominated by consideration of the central tendency rather than variability of export, often restricted to a time frame of < 1 year or stable (baseflow) conditions [but see *Alexander, et al.*, 1996; but see *Goolsby and Battaglin*, 2001]. However, broad deviations in annual river export are ecologically and perhaps evolutionarily relevant, especially for agricultural or urban catchments that are prone to elemental accumulation followed by precipitation-induced flushing. From a water quality standpoint, management strategies geared toward “normal” conditions are not alone sufficient, especially where occasional but highly undesirable conditions are likely to return. We have shown that over a broad time horizon, both the central tendency (median) and inter-annual variability (CV) of river mass export are strongly linked to anthropogenic land use. However, landscape-CV relationships were weaker than landscape-median relationships, which suggests the export CV (and extreme deviations in export) are more explainable from meteorological variability than landscape characteristics. Nonetheless, composition of the terrestrial landscape imposes constraints on river deliveries of water and constituents, and could help predict the risk of export deviations when prior knowledge is lacking. Similarly, an understanding of terrestrial landscape composition may provide a basis for assessing river export responses to changing land use and climate.

Aquatic influences on river export

Lentic water bodies been linked to broadscale (regional or larger) biogeochemical cycles only recently [*Downing*, 2010; *Harrison, et al.*, 2009; *Seitzinger, et al.*, 2005]. However, decades of limnological research indicates important biogeochemical processes within lakes that should influence rivers, when permitted by lake-river connectivity. For example, settlement of organic and particulate phosphorus in lakes removes this nutrient from productive layers [*Essington and Carpenter*, 2000; *Schindler, et al.*, 1993; *Wodka, et al.*, 1985], while denitrification can occur in lakes [*Molot and Dillon*, 1993]. Reservoirs also have broad-scale influences on solute transport, not restricted to phosphrous or nitrogen [*Kelly*, 2001]. Overall, we have shown that lentic water bodies are important components of river basins that affect both the central tendency and variability of river export over a broad time horizon. The collective role of lakes and reservoirs, in short, is to reduce annual mass export and dampen inter-annual variability. In some cases, the influence of lentic water bodies may be comparable to the influence of agriculture (e.g., yield of TSS in this study). Future research is needed to understand competing terrestrial-aquatic influences on river export, and the interaction with climate. We point to the relationship between flow-weighted concentration and water yield (C~Q) as a potentially powerful basis for understanding the river export regime. Fig. 4 shows differences in C~Q slope, as well as the strength of this relationship, for contrasting catchment classes. CV_Y, and in turn the propensity for large deviations in yield, appears highly sensitive to CQ slope (Appendix C).

Meteorology

Meteorological variability, in contrast to climate change or land use change, is not a distant future phenomenon. Rather, it is a current source of inter-annual variability in river export with immediate management ramifications. Recent work on river export has emphasized an interaction between meteorology and landscape factors [*Gascuel-Odoux, et al.*, 2010; *Kaushal, et al.*, 2008; *Lehrter*, 2006; *Martin, et al.*, 2004]. This interaction dictates broadscale river deliveries of water and fertilizing nutrients. While there were some modest long-term trends in yield found in this work- mostly decreases likely associated with altered land management- the range for yield even over a <5 year period was typically larger than the trend amplitude. Similarly, the absence of statistically significant long-term trends in yield at most river sites is partly a consequence of high inter-annual variability relative to long-term changes. Overall, projections of climate variability, especially precipitation variability, may be very important considerations dictating future river export and terrestrial-aquatic linkages.

Future prospects

Over recent decades, expansion of agriculture has corresponded with major hydrologic alterations including wetland destruction and dam construction. Currently, tradeoffs between agricultural resources and water resources are occurring in several regions of the globe, and likely to expand with increasing demands for food and water. In the future, stewardship of these linked food and water resources will require difficult decisions, and would be aided by an improved understanding of inter-annual patterns of river export from catchments. Studies of small- and intermediate-sized catchments will in turn be needed to understand the effects of interacting landscape and meteorological changes on rivers. This is because catchments aggregate reach-scale and landscape processes into tractable river signals that might realistically feedback upon management, and unlike large rivers are not diluted by a complex array of confounding natural and anthropogenic influences.

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Table 1. Metrics and notation.

Metric	Units	Description
Y_t	$M\ L^{-2}\ t^{-1}$	Year-specific mass yield
Q_t	$L\ t^{-1}$	Year-specific water yield
C_t	$M\ L^{-3}\ t^{-1}$	Year-specific flow-weighted annual concentration (Y_t/Q_t)
$\widetilde{Y}$	$M\ L^{-2}\ t^{-1}$	Median mass yield
$\widetilde{Q}$	$L\ t^{-1}$	Median water yield
$\widetilde{C}$	$M\ L^{-2}\ t^{-1}$	Median flow-weighted annual concentration
CV_Y	unitless	Mass yield CV
CV_Q	unitless	Water yield CV
CV_C	unitless	Flow-weighted annual concentration CV

Table 2. Central tendency and variability of river export for contrasting catchment classes (*AQUA*×*LAND*). Inter-catchment means are at bottom.

Form	*AQUA*	*LAND*	$\widetilde{Y}$	CV_Y	$\widetilde{C}$	CV_C	$\widetilde{Q}$	CV_Q	n
TN	*lotic*	*forested*	176	0.26	0.62	0.05	0.29	0.22	6
		mixed	763	0.33	3.13	0.06	0.25	0.30	16
		agricultural	1766	0.42	4.88	0.11	0.34	0.37	9
	lentic	*forested*	268	0.22	0.95	0.02	0.28	0.22	4
		mixed	340	0.26	1.33	0.04	0.25	0.23	4
		agricultural	720	0.35	2.92	0.06	0.26	0.35	6
TP	*lotic*	*forested*	12	0.31	0.04	0.09	0.29	0.22	6
		mixed	72	0.60	0.35	0.25	0.25	0.36	20
		agricultural	119	0.61	0.63	0.20	0.28	0.42	14
	lentic	*forested*	12	0.21	0.04	0.04	0.27	0.19	7
		mixed	46	0.29	0.17	0.10	0.26	0.21	8
		agricultural	40	0.41	0.17	0.09	0.25	0.36	8
TSS	*lotic*	*forested*	9735	0.36	32.09	0.15	0.29	0.22	6
		mixed	22047	0.74	114.40	0.42	0.25	0.37	18
		agricultural	27227	0.92	107.50	0.58	0.29	0.40	13
	lentic	*forested*	917	0.23	3.44	0.05	0.27	0.22	3
		mixed	4979	0.35	17.85	0.19	0.26	0.20	7
		agricultural	9102	0.60	39.86	0.27	0.25	0.36	8
TN	-	-	663	0.30	2.18	0.05	0.28	0.27	45
TP	-	-	50	0.40	0.23	0.13	0.27	0.29	63
TSS	-	-	12334	0.53	52.52	0.28	0.27	0.30	55

Table 3. ANOVA tables for the central tendency and variability of river exports in relation to terrestrial landscape composition (*LAND*) and aquatic composition (*AQUA*).

		A. TN							B. TP							C. TSS						
Form	Metric	Factor	Df	SS	MS	F	*p*	partial r^2	Factor	Df	SS	MS	F	*p*	partial r^2	Factor	Df	SS	MS	F	*p*	partial r^2
TN	$\log 10 \tilde{Y}$	*AQUA*	1	0.26	0.26	4.57	**0.039**	0.04	*AQUA*	1	1.16	1.16	8.98	**0.004**	0.08	*AQUA*	1	2.90	2.90	15.27	**<0.001**	0.18
		LAND	2	3.35	1.68	30.04	**<0.001**	0.55	*LAND*	2	4.77	2.39	18.45	**<0.001**	0.35	*LAND*	2	2.88	1.44	7.58	**0.001**	0.18
		AQUA:LAND	2	0.29	0.15	2.60	0.087	0.05	*AQUA:LAND*	2	0.24	0.12	0.91	0.407	0.02	*AQUA:LAND*	2	0.56	0.28	1.48	0.237	0.04
		Residuals	40	2.23	0.06				Residuals	58	7.50	0.13				Residuals	50	9.49	0.19			
	$\tilde{C}$	*AQUA*	1	13.37	13.37	5.91	**0.020**	0.07	*AQUA*	1	1.04	1.04	3.61	0.063	0.05	*AQUA*	1	62695	62695	8.05	**0.007**	0.13
		LAND	2	73.61	36.80	16.27	**<0.001**	0.39	*LAND*	2	1.28	0.64	2.21	0.119	0.07	*LAND*	2	32824	16412	2.11	0.132	0.07
		AQUA:LAND	2	9.11	4.56	2.01	0.147	0.05	*AQUA:LAND*	2	0.47	0.23	0.81	0.448	0.02	*AQUA:LAND*	2	7068	3534	0.45	0.638	0.01
		Residuals	40	90.51	2.26				Residuals	58	16.74	0.29				Residuals	50	389223	7784			
	CV_Y	*AQUA*	1	0.03	0.03	2.19	0.147	0.04	*AQUA*	1	0.88	0.88	12.66	**0.001**	0.16	*AQUA*	1	1.02	1.02	6.94	**0.011**	0.10
		LAND	2	0.14	0.07	5.47	**0.008**	0.21	*LAND*	2	0.55	0.27	3.91	**0.026**	0.10	*LAND*	2	1.71	0.86	5.80	**0.005**	0.17
		AQUA:LAND	2	0.00	0.00	0.05	0.952	0.00	*AQUA:LAND*	2	0.09	0.05	0.67	0.513	0.02	*AQUA:LAND*	2	0.11	0.05	0.36	0.697	0.01
		Residuals	40	0.52	0.01				Residuals	58	4.04	0.07				Residuals	50	7.38	0.15			
	CV_C	*AQUA*	1	0.01	0.01	4.33	**0.044**	0.08	*AQUA*	1	0.24	0.24	8.26	**0.006**	0.12	*AQUA*	1	0.62	0.62	3.49	0.067	0.06
		LAND	2	0.02	0.01	5.40	**0.008**	0.19	*LAND*	2	0.12	0.06	2.08	0.134	0.06	*LAND*	2	0.90	0.45	2.55	0.088	0.09
		AQUA:LAND	2	0.00	0.00	0.74	0.484	0.03	*AQUA:LAND*	2	0.02	0.01	0.35	0.710	0.01	*AQUA:LAND*	2	0.06	0.03	0.18	0.839	0.01
		Residuals	40	0.07	0.00				Residuals	58	1.68	0.03				Residuals	50	8.83	0.18			
	$\tilde{Q}$	*AQUA*	1	0.01	0.01	0.30	0.585	0.01	*AQUA*	1	0.00	0.00	0.05	0.816	0.00	*AQUA*	1	0.00	0.00	0.16	0.692	0.00
		LAND	2	0.03	0.02	0.75	0.479	0.04	*LAND*	2	0.01	0.00	0.25	0.777	0.01	*LAND*	2	0.01	0.00	0.22	0.803	0.01
		AQUA:LAND	2	0.01	0.01	0.27	0.769	0.01	*AQUA:LAND*	2	0.01	0.00	0.13	0.877		*AQUA:LAND*	2	0.01	0.00	0.17	0.844	0.01
		Residuals	40	0.91	0.02				Residuals	58	1.11	0.02				Residuals	50	1.02	0.02			
	CV_Q	*AQUA*	1	0.01	0.01	0.58	0.451	0.01	*AQUA*	1	0.15	0.15	10.57	**0.002**	0.12	*AQUA*	1	0.07	0.07	4.86	**0.032**	0.07
		LAND	2	0.13	0.06	6.70	**0.003**	0.24	*LAND*	2	0.28	0.14	9.99	**<0.001**	0.22	*LAND*	2	0.21	0.10	6.92	**0.002**	0.19
		AQUA:LAND	2	0.01	0.00	0.48	0.623	0.02	*AQUA:LAND*	2	0.04	0.02	1.39	0.257	0.03	*AQUA:LAND*	2	0.05	0.03	1.83	0.171	0.05
		Residuals	40	0.38	0.01				Residuals	58	0.80	0.01				Residuals	50	0.74	0.01			

Table 4. Cross-catchment differences in the central tendency of river exports. Median mass yield ($\widetilde{Y}$) and median flow-weighted concentration ($\widetilde{C}$) of TN, TP, and TSS are shown. Significant p values are in bold, marginally significant (≤0.075) are underlined. Differences in $\widetilde{Q}$ among catchment classes were not significant.

Form	Metric	Factor	Comparison	Mean diff.	Lower conf. limit	Upper conf. limit	*p*
TN	$\log 10\ \widetilde{Y}$	*AQUA*	*lentic-lotic*	-0.16	-0.31	-0.01	0.039
		LAND	*mixed-forested*	0.43	0.21	0.65	<0.001
			agricultural-forested	0.73	0.50	0.95	<0.001
			agricultural-mixed	0.30	0.10	0.49	0.002
	$\widetilde{C}$	*AQUA*	*lentic-lotic*	-1.17	-2.15	-0.20	0.020
		LAND	*mixed-forested*	1.83	0.46	3.21	0.006
			agricultural-forested	3.40	1.95	4.85	<0.001
			agricultural-mixed	1.56	0.31	2.81	0.011
TP	$\log 10\ \widetilde{Y}$	*AQUA*	*lentic-lotic*	-0.28	-0.47	-0.09	0.004
		LAND	*mixed-forested*	0.60	0.32	0.89	<0.001
			agricultural-forested	0.70	0.40	1.00	<0.001
	$\widetilde{C}$	*AQUA*	*lentic-lotic*	-0.27	-0.55	0.01	0.062
TSS	$\log 10\ \widetilde{Y}$	*AQUA*	*lentic-lotic*	-0.49	-0.74	-0.24	<0.001
		LAND	*mixed-forested*	0.48	0.09	0.87	0.013
			agricultural-forested	0.65	0.24	1.05	0.001
	$\widetilde{C}$	*AQUA*	*lentic-lotic*	-71.64	-122.35	-20.94	0.007

Table 5. Cross-catchment differences for the inter-annual variability river exports. CV of mass yield (CV_Y) and flow-weighted concentration (CV_C) for TN, TP, and TSS are shown. Water yield variability (CV_Q) is also shown. Significant p values are in bold, marginally significant are underlined.

Form	Metric	Factor	Comparison	Mean diff.	Lower conf. limit	Upper conf. limit	*p*
TN	CV_Y	*LAND*	*agricultural-forested*	0.15	0.04	0.26	0.007
	CV_C	*AQUA*	*lentic-lotic*	-0.03	-0.05	0.00	0.044
			agricultural-forested	0.05	0.01	0.09	0.014
			agricultural-mixed	0.04	0.00	0.07	0.030
	CV_Q	*LAND*	*agricultural-forested*	0.14	0.05	0.23	0.002
			agricultural-mixed	0.07	-0.01	0.16	0.075
TP	CV_Y	*AQUA*	*lentic-lotic*	-0.24	-0.38	-0.11	0.001
		LAND	*mixed-forested*	0.19	-0.01	0.40	0.071
			agricultural-forested	0.24	0.02	0.46	0.026
	CV_C	*AQUA*	*lentic-lotic*	-0.13	-0.22	-0.04	0.006
	CV_Q	*AQUA*	*lentic-lotic*	-0.10	-0.16	-0.04	0.002
		LAND	*mixed-forested*	0.09	-0.01	0.18	0.069
			agricultural-forested	0.18	0.08	0.27	<0.001
			agricultural-mixed	0.09	0.01	0.17	0.026
TSS	CV_Y	*AQUA*	*lentic-lotic*	-0.29	-0.51	-0.07	0.011
			agricultural-forested	0.50	0.14	0.86	0.004
	CV_C	*AQUA*	*lentic-lotic*	-0.22	-0.47	0.02	0.067
		LAND	*agricultural-forested*	0.36	-0.03	0.75	0.073
	CV_Q	*AQUA*	*lentic-lotic*	-0.08	-0.15	-0.01	0.032
		LAND	*agricultural-forested*	0.17	0.06	0.29	0.002

Figure Legends

Figure 1. Map of Wisconsin long-term river sites.

Figure 2. Examples of TP yield time series for contrasting catchment classes. The period of record from 1986 to 2006 was used to calculate median mass yield (g $\mathrm{km^{-2}\ yr^{-1}}$), median flow-weighted annual concentration, median water yield, and CV's for each of those. Key: squares=*agricultural*; triangles=*forested*; white=*lotic*; black=*lentic*. *Mixed* examples not shown.

Figure 3. Median annual mass yield ($\widetilde{Y}$, g $\mathrm{km^{-2}\ y^{-1}}$) and range for river TP, TN, TSS, as well as median water yield ($\widetilde{Q}$, m) for contrasting Wisconsin catchments. Key: squares=*agricultural*; circles=*mixed*, triangles=*forested*; white=*lotic*; black=*lentic*.

Figure 4. Contrasting relationship types for flow-weighted annual concentration (C_t, mg $\mathrm{L^{-1}}$) of total nitrogen (TN) and water yield (Q_t, m). Relationship types shown include strong positive (concentrating), weak positive, no relationship, and strong negative (diluting). Data are from stream/river sites during water years 1986-2006. Upper left= *agricultural-lotic*; upper right=*agricultural-lentic*; lower left=*agricultural-lotic*; lower right=*forested-lotic*.

Figure 1.

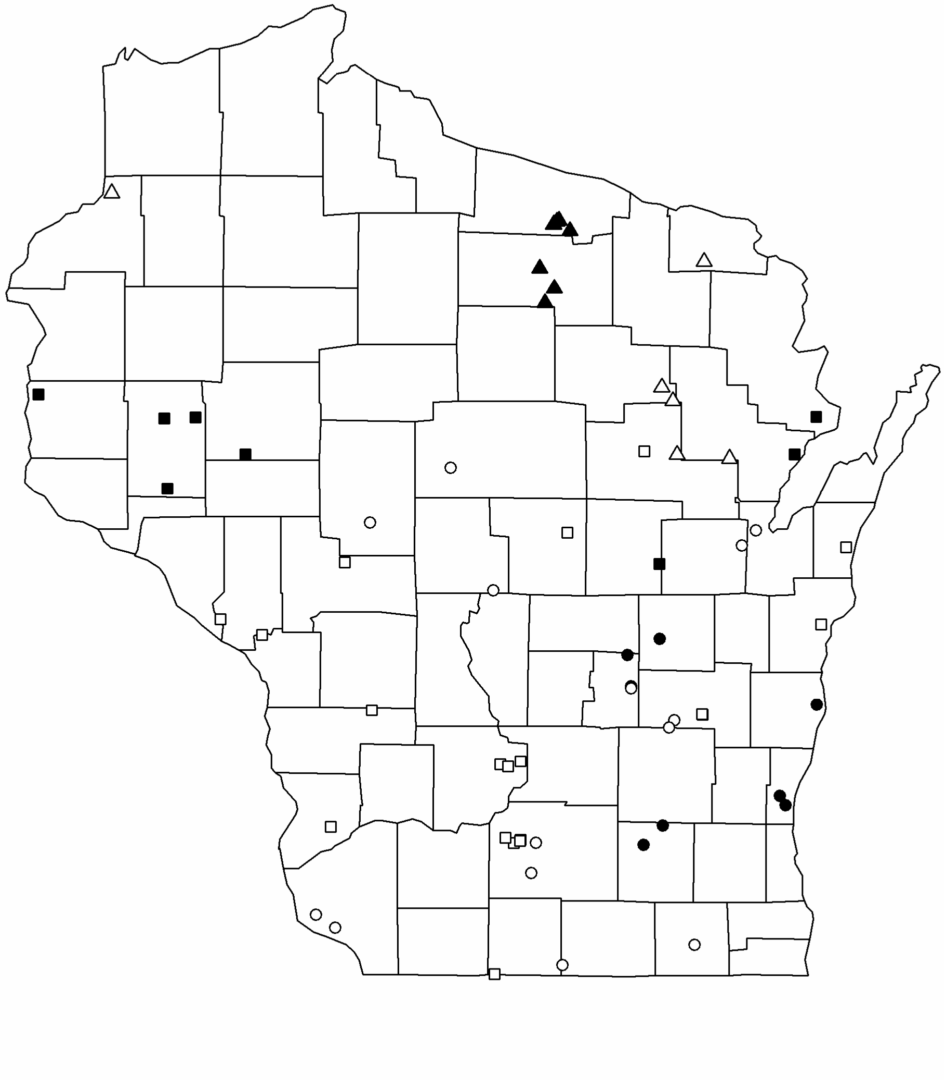


Figure 2.

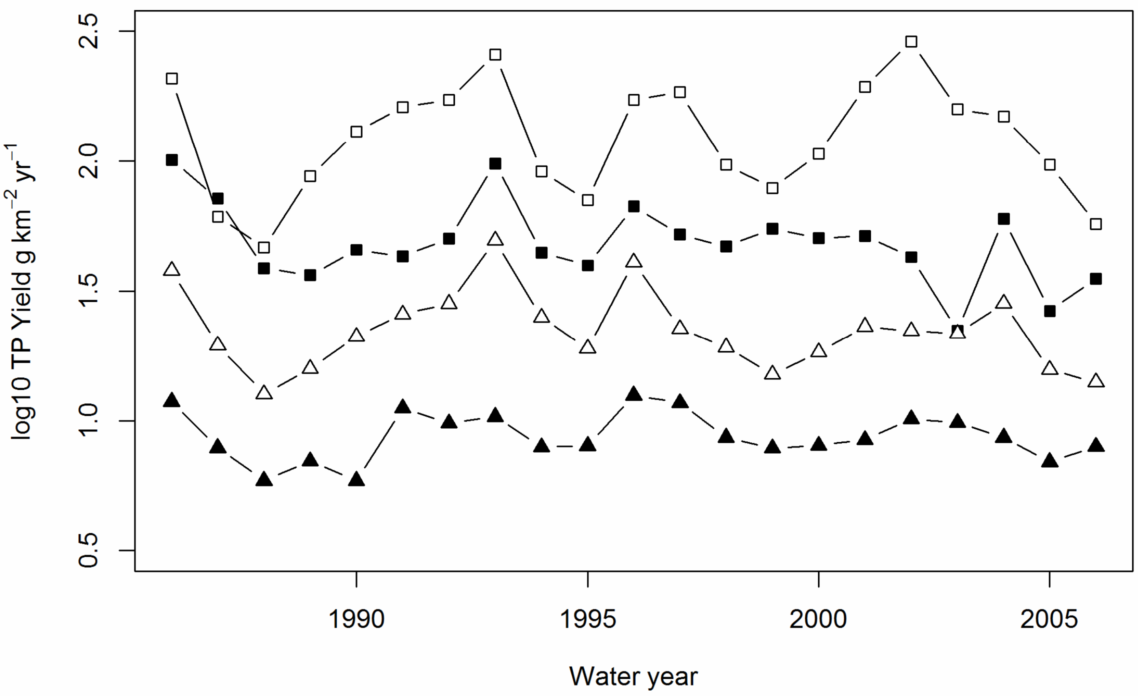

log10 TP Yield g km^{-2} yr^{-1}
0.5
1.0
1.5
2.0
2.5
1990
1995
2000
2005
Water year

Figure 3.

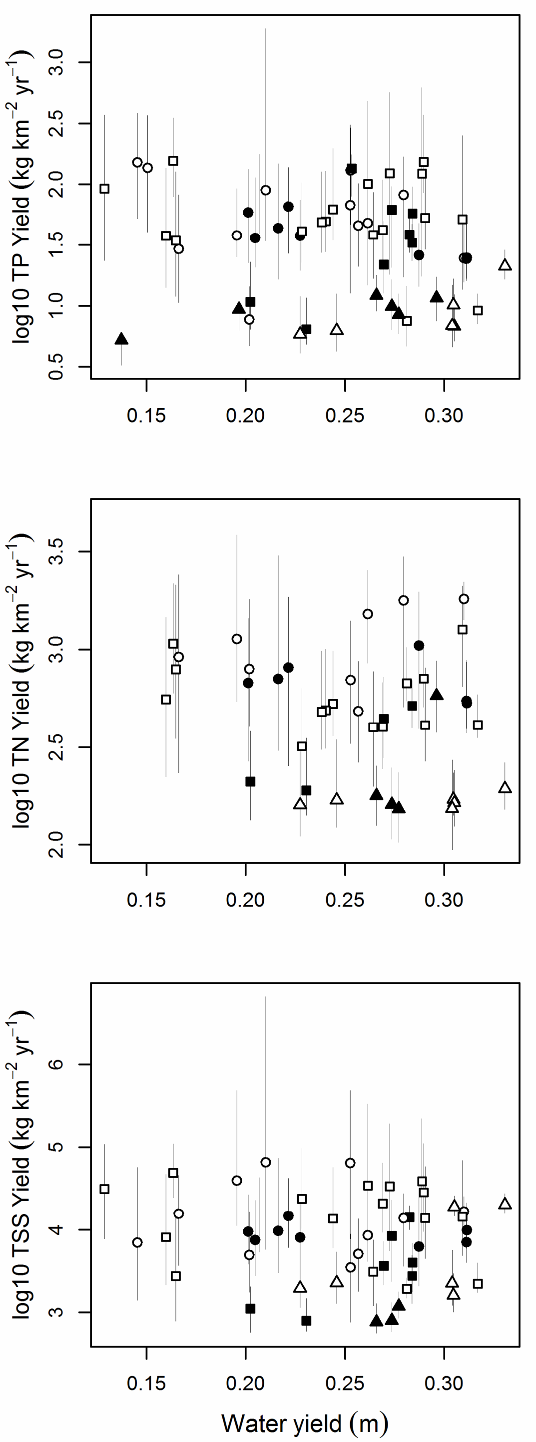
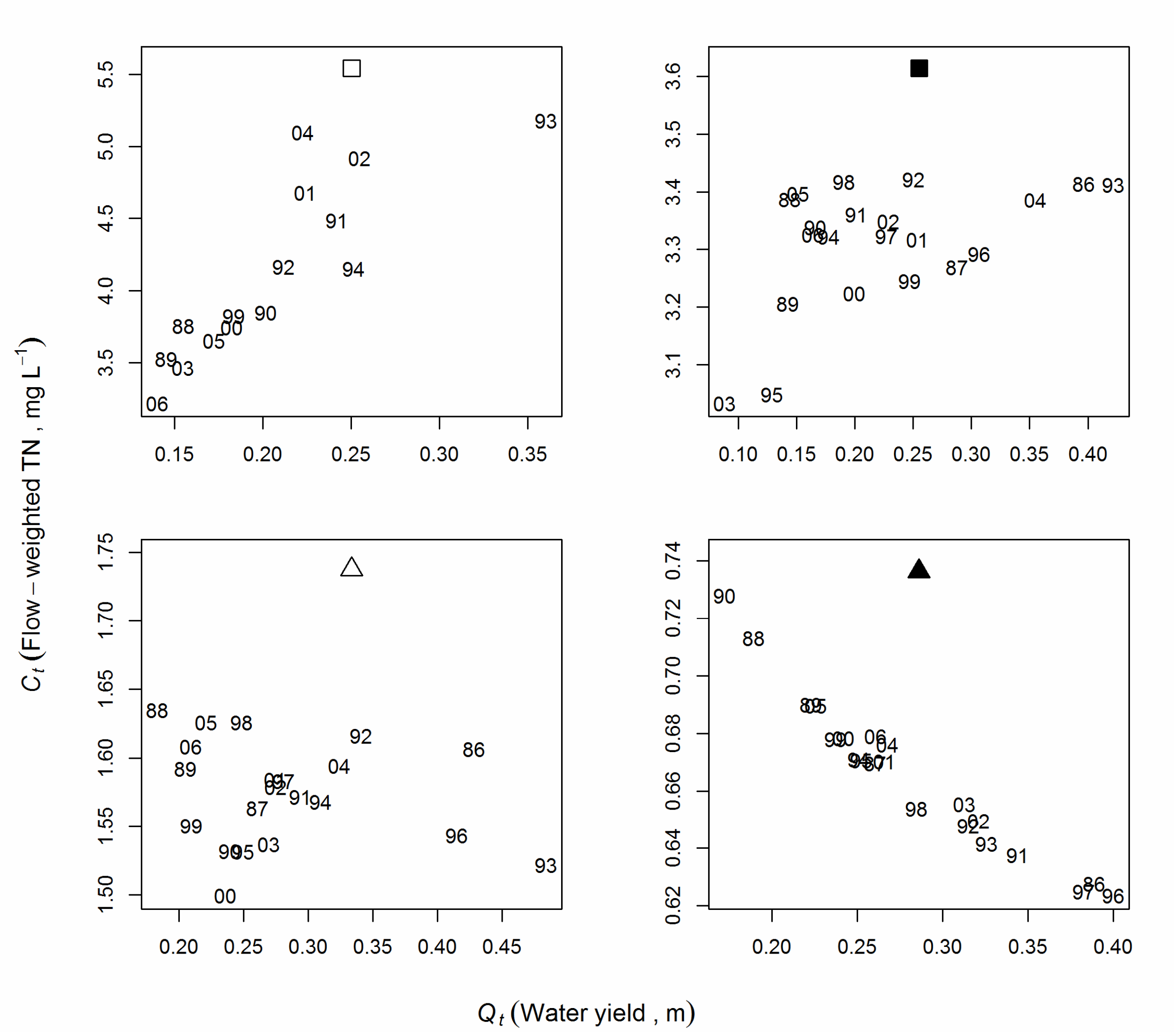

log10 TP Yield (kg km^{-2} yr^{-1})
0.5
1.0
1.5
2.0
2.5
3.0
0.15
0.20
0.25
0.30
log10 TN Yield (kg km^{-2} yr^{-1})
2.0
2.5
3.0
3.5
0.15
0.20
0.25
0.30
log10 TSS Yield (kg km^{-2} yr^{-1})
3
4
5
6
0.15
0.20
0.25
0.30
Water yield (m)

Figure 4.



Appendix C. Estimation of annual loads, and supporting materials

Annual loads were estimated using methods similar to those of Saad et al. [2011] which in turn were based on regression methods of Cohn [2005]. The load estimates incorporate two models: a water-quality model and a flow model used to remove trends in streamflow. The water-quality model (Equation 1) relates the logarithm of concentration at time t (c_t) to the logarithm of daily flow (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),

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

where b_0, b_q, b_T, b_s, and b_c are fixed coefficients estimated by the adjusted maximum likelihood method (Cohn, 2005), and e_t is assumed to be independent and normally distributed with mean 0 and variance σ_e^2. Daily loads (l_t, M T^{-1}) for each site were in turn estimated from $c_t \times q_t$, and summed for each water year to estimate annual loads (L_t) between 1986 and 2006.

Sites with long-term trends in river yield (Y_t) are shown in Table A. Land use cross-correlation plots are shown in Figure A. The sensitivity of CV_Y to CQ slope (m_{CQ}) is shown in Figure B.

References (Appendix C)

Cohn TA (2005) Estimating contaminant loads in rivers: An application of adjusted maximum likelihood to type 1 censored data. Water Resources Research 41:

Saad DA, Schwarz GE, Robertson DM & Booth NL (2011) A multi-agency nutrient dataset used to estimate loads, improve monitoring design, and calibrate regional nutrient SPARROW models. Journal of the American Water Resources Association 47: 933-949

Table A. Sites showing long-term log-linear trends in river yield (Y_t). Only sites with long-term trends >50% (positive or negative) are shown.

Trend direction	Var	n_t	Site No.	Slope (m) ± s.e.	p-value (slope)	% change
negative	TN	21	5431017	-0.025 ± 0.009	0.01	-68
		21	4087120	-0.016 ± 0.005	0.00	-53
	TP	21	413002	-0.038 ± 0.004	0.00	-82
		21	543056	-0.033 ± 0.000	0.00	-78
		18	4086500	-0.034 ± 0.006	0.00	-73
		21	523061	-0.028 ± 0.006	0.00	-72
		21	5430175	-0.026 ± 0.003	0.00	-70
		21	4087120	-0.022 ± 0.006	0.00	-63
		17	5427900	-0.027 ± 0.010	0.01	-63
		18	313038	-0.022 ± 0.010	0.05	-58
		21	5406491	-0.018 ± 0.006	0.01	-56
		21	683096	-0.018 ± 0.004	0.00	-56
	TSS	21	5431017	-0.109 ± 0.009	0.00	-99
		17	4080798	-0.060 ± 0.003	0.00	-89
		14	4077630	-0.056 ± 0.008	0.00	-81
		18	313038	-0.038 ± 0.013	0.01	-77
		21	503059	-0.028 ± 0.007	0.00	-72
		21	373325	-0.026 ± 0.010	0.02	-70
		21	5431486	-0.026 ± 0.012	0.04	-70
positive	TN	21	173208	0.009 ± 0.003	0.00	53
		21	5427948	0.022 ± 0.007	0.01	174
	TP	21	5427952	0.029 ± 0.012	0.03	272
	TSS	21	5430175	0.012 ± 0.006	0.04	75
		18	4072050	0.035 ± 0.014	0.02	290
		21	4087159	0.033 ± 0.012	0.01	365

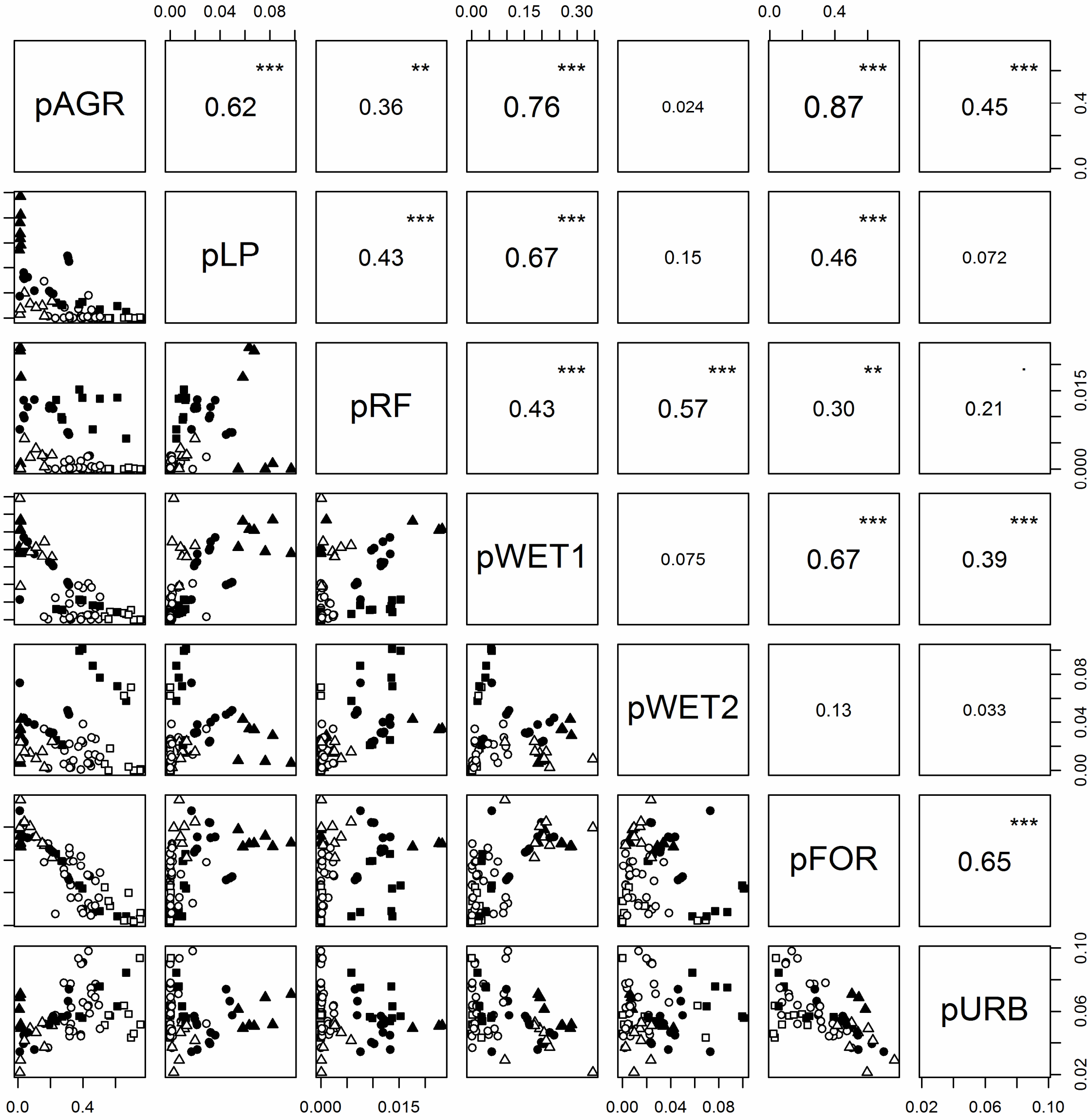


Figure A. Cross-correlation plots of catchment landscape characteristics for stream and river sites in Wisconsin. The National Land Cover Dataset (2001) and Wisconsin Hydrography Dataset (2006) were used. Stars indicate the level of significance (**, p≤0.01; ***, p=0.001).

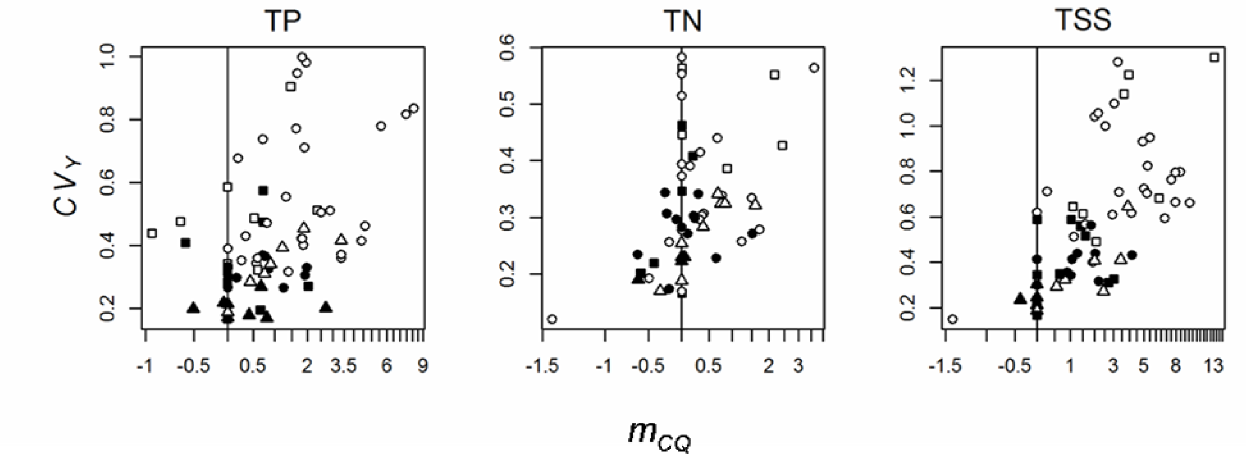


Figure B. Relationships between inter-annual variability of river mass yields (CV_Y) and slope of the relationship between flow-weighted mean annual concentration and water yield (C~Q slope, m_{CQ}). m_{CQ} is standardized to the median yield ($m_{CQ} = m/\widetilde{Y}$, where m is the raw C~Q slope), which enables a more straightforward comparison across constituent forms. Non-significant slopes are plotted along the zero vertical.

CHAPTER 5

SYNTHESIS, CROSS-SCALE RESEARCH, AND FUTURE PROSPECTS

The spatial and temporal scales of observation differ markedly among the previous chapters, and these scale differences must be recognized when interpreting the dissertation. While scale-dependency of findings is a well established idea, I am not satisfied that I have properly addressed it elsewhere, so will make an attempt. Here, I discuss scale issues in an effort to a) synthesize the chapters, b) promote their responsible interpretation, and c) identify some scale-dependencies that might feed into cross-scale research. I hope this effort will prevent the mistaken substitution of findings to inappropriate scales outside those of the researched phenomena. Let me also offer that a cross-scale research component could be judged as the missing piece of my dissertation.

First, I will discuss one clear example of a scale-sensitive result from this dissertation. In the abstract of chapter 2, I state: *SLOW subreaches had 45% lower ecosystem-level uptake rate (K, t^{-1}) on average, indicating reduced uptake efficiency in flow-through wetlands relative to streams*. Upon more than a year’s worth of reflection about this result, I am increasingly convinced that the lower uptake efficiency of wetlands relative to streams should indeed be broadly true for baseflow periods at this temporal extent (warm season) regardless of the nutrient form (nitrate, ammonium, dissolved inorganic P). However, at least in the case of nitrogen, the statement is assuredly false at a longer temporal grain- such as for measurements of total annual nitrogen input relative to output- when denitrification should be the dominant process affecting the nitrogen balance. Stated another way, the result of higher uptake efficiency of streams is contingent upon the strong dominance of total mass uptake by benthic algae; thus, it should not apply in the absence of net algal uptake (and net biomass accrual), as might occur when the temporal extent of observations includes periods of net mineralization (~fall turnover) or when the temporal grain of observation is large enough to incorporate such dynamics. It is also very important to recognize that low uptake efficiency (K or v_f) can still result in high mass uptake if water residence time is high (Figure 1).

Second, I will declare explicitly the spatio-temporal scales of each chapter. In chapter 2 (Nutrient retention and the problem of hydrologic disconnection in streams and wetlands), the temporal grain of observation is equal to water residence time of the ecosystem (minutes to hours) and so varies slightly among the study reaches, while the temporal extent is the study season (weeks to months, warm season only). In chapter 3 (Altered stream chemistry following the loss of a mature agricultural impoundment), the temporal grain of observation is similar to the previous chapter (minutes to hours), but the temporal extent is substantially longer (the period of record, 6 years). In chapter 4 (Agricultural and aquatic contributions to inter-annual variability of river export), the temporal scale is much different compared to both chapters 2 and 3. Temporal grain and temporal extent in chapter 4 are both fixed (one water year, and 21 water years, respectively). For spatial scales, in chapter 2 the spatial grain of observation is the reach (meters to kilometers) while the spatial extent is, approximately, the Northern Highlands Lake District. In chapter 3, which was not spatially explicit, the spatial grain of observation and the spatial extent are both the river reach (meters to kilometers). In chapter 4, the spatial grain of observation is the catchment, while the spatial extent is, approximately, the state of Wisconsin.

What cross-scale patterns should we expect? *The range and variance of a biogeochemical process may be generally expected to decrease with increasing grain of observation*. The landscape ecologist knows this as the “spatial aggregation effect” and the idea is also applicable over time. For example, if we examine monthly water yield and annual water yield over a 10 year period of record at one river site, the variance and range of annual water yield will be lower, essentially due to offsetting by high and low monthly values within each year. As I detail below, when the temporal grain of observation shifts from a short time interval (hours to days) to a long time interval (years to decades), the rate of variability decline may differ among ecosystem types.

Some further questions: 1) What is the upper rate limit (“optimum”) for a biogeochemical process within the ecosystem? 2) How often does the ecosystem operate at this optimum rate? 3) How does the broader process regime- the entire frequency distribution of rates over time- vary among ecosystem types? Even when standardized to a common nutrient load or background concentration, I expect the answers to these questions to differ largely among ecosystem types, due to differences in the suite of mechanisms present (assimilation by benthic algae, assimilation by phytoplankton, denitrification, particle settling). Figure 2 shows some predictions of cross-ecosystem and cross-scale differences in optimum, focusing on uptake of nitrogen. With an expanding temporal grain, the rate of decrease for the process optimum should be largest for streams due to highly efficient short-term uptake but lack of long-term mechanisms of nitrogen removal (denitrification). There remains a need to compare similar scale dependencies across ecosystem types.

A comment on the implications of short-term vs. long-term biogeochemical processes

Within an integrative field such as ecology, there is sometimes an inclination to push toward an understanding of the longer- and longer-term phenomena. In part, this is good, because frontiers often lie at the broader scales, and because this understanding is needed for long-term management. However, it would be irresponsible to divert all resources toward long-term management strategies that have yet to be proven. Therefore, in the quest for a long-term solution to cultural eutrophication (a socio-economic problem that probably requires a socio-economic solution) it is important to recognize additional strategies that might provide even modest short-term improvements, or damage control. In the proceeding section, I discuss some modest management implications of short-term, seasonal uptake by benthic algae (central to Chapters 2 and 3) which should not be dismissed as unimportant.

Take for example a representative passage from the reply to a recent controversial paper by Cardinale [2011]:

> "…because benthic algae do not accumulate over long (annual or interannual) periods, this uptake mechanism represents only a transient storage pool and thus has no enduring effect on downstream water quality" [*Baulch, et al.*, 2011].

The Cardinale paper is problematic, only partly because it proposes an irresponsible association between biodiversity and ecosystem functioning (nutrient retention increases with species richness) when established theory provides the responsible explanation [increase with net biomass increment; *Vitousek and Reiners*, 1975]. But in river basins with culturally eutrophied waters, uptake by biofilms and macrophytes still has a modest value because these storage pools often persist from weeks to months, delaying nutrient transport (from weeks to months). In other words, within river networks, every atom of nitrogen uptaken by an algal cell during warm months represents one less nitrogen atom delivered to a downstream ecosystem during the most active period of aquatic productivity. Consequently, riparian canopy thinning might be viewed as a strategy to promote nutrient delay through increased benthic production. Continued increases in benthic production will also inevitably occur within numerous reservoirs as they continue to lose depth through sedimentation. Nonetheless, it has yet to be shown whether managed increases in benthic production could be sufficient to decrease warm-season nutrient deliveries to downstream waters.

Through my dissertation, I have identified several areas of potential future research, which I limit here to my favorite three questions. The first is directly linked to chapter 3, and may be best examined at a continental or global extent: how does aging influence the biogeochemical role of impoundments? The second is linked to chapter 4, and may best be examined using CQ relationships: from which catchments should we anticipate disproportionately high N/P/sediment transport on the recovery from drought? The third provides a basis for cross-system comparison (wetlands and reservoirs): what ecosystem structure (mixing regime, bathymetry, morphometry) maximizes annual rates of denitrification, and possibly, methane production?

References

Baulch, H. M., E. H. Stanley, and E. S. Bernhardt. 2011. Can algal uptake stop NO3- pollution? Nature **47**.

Cardinale, B. J. 2011. Biodiversity improves water quality through niche partitioning. Nature **472**:86-89.

Vitousek, P. M., and W. A. Reiners. 1975. Ecosystem succession and nutrient retention - hypothesis. Bioscience **25**:376-381.

Figure Legends

Figure 1. Theoretical relationship between P (proportion of mass inputs taken up) and mean water residence time. The plotted points provide a clarification of Chapter 2 results: an ecosystem with lower uptake efficiency (dashed line) may still yield higher *P* than an ecosystem with higher uptake efficiency (solid line) if water residence time is higher. This is demonstrated by higher *P* for the black point compared to the white point. Note that higher *P* will also translate to higher mass uptake (output mass minus input mass) when inputs are similar. Mean water residence time is often a proxy for ecosystem size.

Figure 2. Predicted cross-ecosystem and cross-scale differences in maximum uptake efficiency for dissolved nitrogen. A general decrease in maximum uptake (optimum) is predicted with an increasing temporal grain of observation, although the rate of decline may differ among ecosystem types. Thus, it is possible for streams to have both higher short-term (hours-to-days) and lower long-term (years-to-decades) uptake efficiency compared to other ecosystem types.

Figure 1.

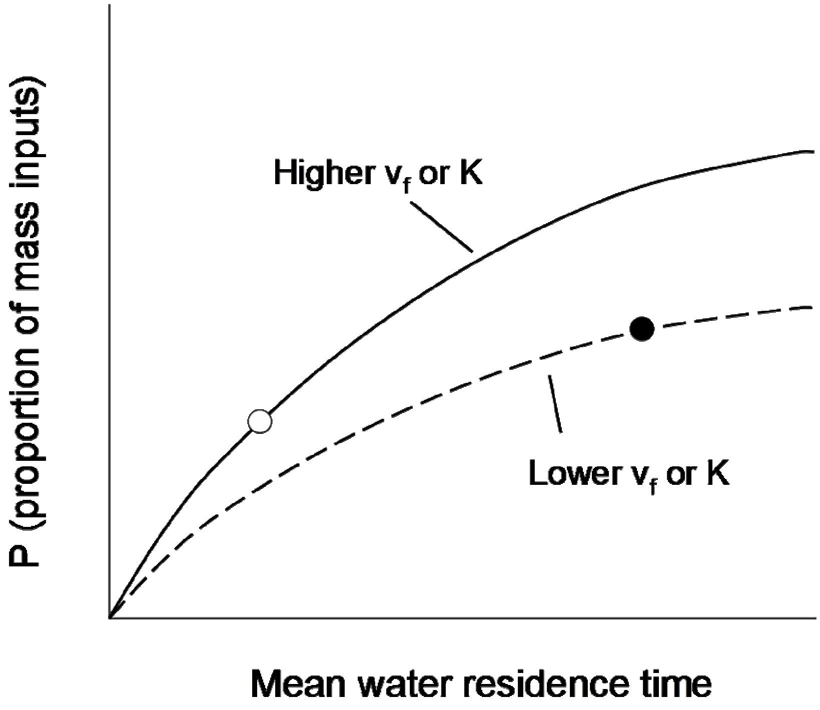
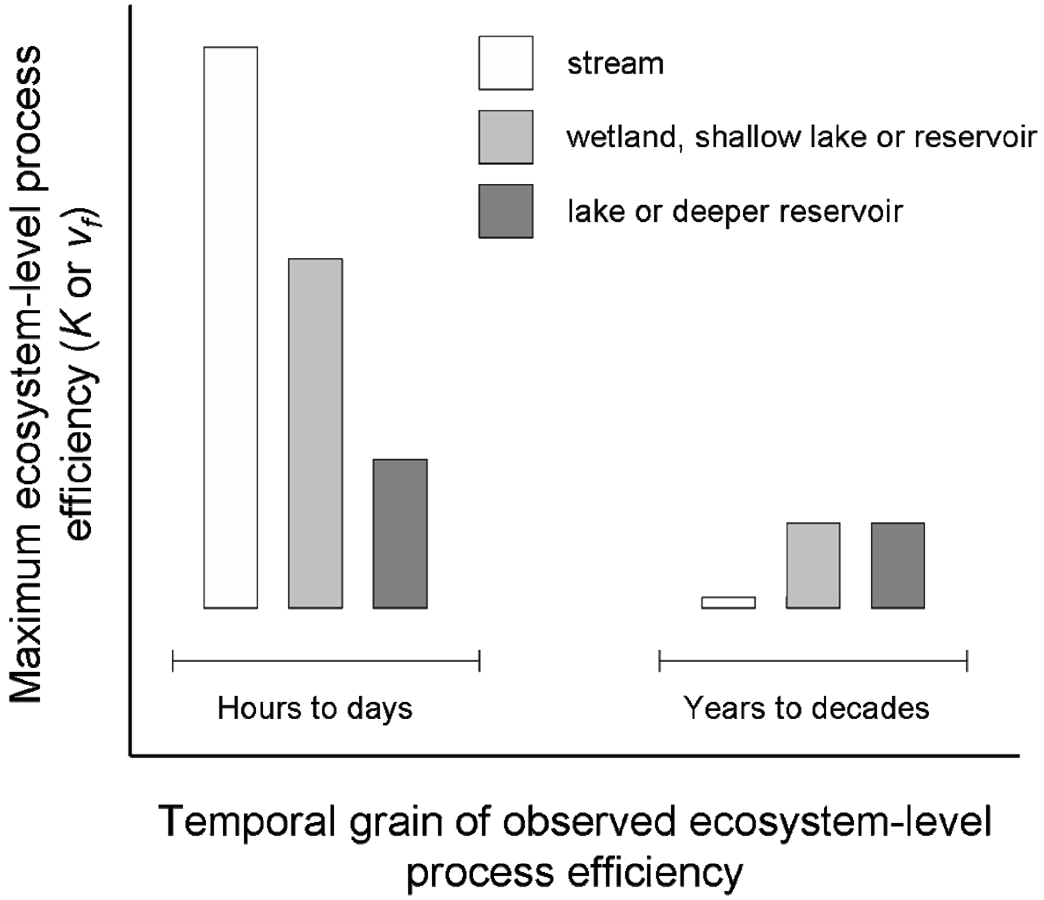

P (proportion of mass inputs)
Higher v_f or K
Lower v_f or K
Mean water residence time

Figure 2.



Maximum ecosystem-level process efficiency (K or v_f)
stream
wetland, shallow lake or reservoir
lake or deeper reservoir
Hours to days
Years to decades
Temporal grain of observed ecosystem-level process efficiency