

Hydrologic and biogeochemical functioning of intensively managed catchments: A synthesis of top-down analyses

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[1] This paper synthesizes a 3-year collaborative effort to characterize the biogeochemical and hydrological features of intensively managed agricultural catchments by combining data analysis, modeling, and preliminary hypothesis testing. The specific focus was on the Midwestern region of the United States. The results suggest that: (1) water management, specifically the homogenization of evapotranspiration losses driven by mono-cultural vegetation cover, and the homogenization of runoff generation driven by artificial drainage, has created engineered, predictable hydrologic systems; (2) nutrient and pesticide management, specifically their regular applications have created two kinds of biogeochemical export regimes: *chemostatic* (low variability in concentration as exhibited by nitrate) and *episodic* (high variability in concentration as exhibited by pesticides); (3) coupled mass-balance models for water and solutes reproduce these two regimes as a function of chemical rate constants. Phosphorus transport regimes were found to be episodic at smaller spatial scales, but chemostatic at larger scales. Chemostatic response dominates in transport-limited catchments that have internal sources of the solute to buffer the periodicity in episodic inputs, while episodic response dominates in source-limited catchments. The shift from episodic nitrate export in pristine catchments to chemostatic regimes in managed watersheds was attributed to legacy stores of nitrogen (built from continued fertilizer applications) that buffer interannual variations in biogeochemical processing. Fast degradation kinetics of pesticides prevents the build-up of legacy sources, and leads to episodic export. Analytical expressions were derived for the probability density functions of solute delivery ratio as a function of the stochastics of rainfall-runoff events and biogeochemical controls.

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1. Introduction

1.1. Motivation

[2] Most catchments around the world are strongly influenced by human activity [Vörösmarty *et al.*, 2010] so that hydrologic and biogeochemical responses reflect both the features of the pristine landscape and its alterations [Vitousek *et al.*, 1997a, 1997b; Weiskel *et al.*, 2007]. In intensively managed catchments, the magnitude and persistence of human intervention is so great that all aspects of the catchment function have been and continue to be impacted. Intense management of catchments is tied to numerous pressing environmental and social issues such as eutrophication

and hypoxia of receiving water bodies [Diaz and Rosenberg, 2008; Kemp *et al.*, 2009; Osterman *et al.*, 2009; Rabalais *et al.*, 1996, 2002; Smith *et al.*, 1999], toxicity associated with pesticide, hormonal and pharmaceutical contamination [Durhan *et al.*, 2006; Fuortes *et al.*, 1997; Soto *et al.*, 2004; Winchester *et al.*, 2009; Kolpin *et al.*, 2002], elevated flood risks [Mutel, 2010; Prestegard *et al.*, 1994], erosion [Stone and Krishnappan, 1997], and altered flow regimes [Schilling and Helmers, 2008; Schilling *et al.*, 2008] which impair aquatic ecology [Carlisle *et al.*, 2010]. These anthropogenic issues are intimately related to hydrology and biogeochemistry, and their interaction, which together determine the fate and transport of water and solutes. It is thus crucial to understand the interplay between hydrological transport and biogeochemical processing in impacted catchments. Research into the hydrology and biogeochemistry of intensively managed catchments extends beyond addressing practical environmental problems. Comparative studies that incorporate managed and pristine sites can also contribute to fundamental understanding of coupled hydrologic and biogeochemical processes.

[3] The Midwestern region of the United States provides an excellent case study of intensively managed catchments. The tile-drained, glaciated landscape of the Upper Midwest

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is essentially anthropogenic, with natural prairie and wetland ecosystems almost entirely converted to corn-soybean agricultural production, which occupies nearly 65% of the contemporary landscape [Potts *et al.*, 2004]. Ecosystem conversion has been accompanied by widespread hydrological change, primarily in the form of artificial drainage which occupies more than 30% of the land area [Schilling and Helmers, 2008; Schilling *et al.*, 2008]. Anthropogenic forcing similarly dominates Midwestern biogeochemical cycles where applied fertilizers, animal manures and pesticides, and removed plant residues control the solute mass balance, overwhelming natural variations [Goolsby *et al.*, 1999]. These alterations of water and nutrient dynamics are clearly linked to high profile environmental and social issues such as the Dead Zone in the Gulf of Mexico [Diaz and Rosenberg, 2008; Rabalais *et al.*, 2002] and flooding throughout the Mississippi River Basin [Mutel, 2010; Prestegard *et al.*, 1994]. Finally, the agricultural landscape in the Upper Midwest is attractive as a case study because of its similarity to other intensively managed agricultural landscapes, notably in the drainage basins of the Baltic Sea, as well as managed catchments in Germany, Denmark, China, and the Netherlands.

1.2. Approach

[4] Significant resources are invested in maintaining or restoring intensively managed catchments. The success of restoration and management depends on reliable predictions of water yield and quality across the space-time scales of interest. There are multiple approaches to developing such predictions, either through “bottom-up” modeling based on sophisticated, spatially distributed models that capture all relevant processes and parameters, or alternatively through “top-down” models based on parsimonious representation of the dominant processes identified from examining long-term data [Bai *et al.*, 2009; Klemes, 1983; Leeder, 2011; Levin, 1992; Sivapalan, 2005; Sivapalan *et al.*, 2003; Wagener *et al.*, 2010].

[5] The objective of this paper is to synthesize research undertaken as part of the intensively managed catchments component of the Hydrological Synthesis Project led by the University of Illinois at Urbana Champaign. This research was strongly motivated by the top-down approach that is based on studying patterns in long term observational data with an attempt to classify catchments, identify the dominant drivers and filters of hydrologic responses for each catchment class, and develop parsimonious models [e.g., Atkinson *et al.*, 2002; Wagener *et al.*, 2007, 2010; Zhang *et al.*, 2008; Merz and Blöschl, 2009]. In contrast bottom-up approaches involve development of detailed mechanistic models for several processes, and then implementing them in a spatially distributed manner over multiple scales of interest. In addition to work done as a part of the Synthesis Project, we also draw on related studies which, although undertaken independently, “cross fertilized” with the Project. Synthesis in this context refers to research that attempts to “aggregate and simplify, retaining essential information without getting bogged down in unnecessary details . . . abstracting and incorporating just enough detail to (explain) the observed patterns” [Levin, 1992]. The research studies therefore began with analyzing data to identify emergent or persistent patterns that were linked to

underlying physical, chemical, or biological processes. The observed patterns inspired hypotheses for mechanistic explanations. Linking pattern to process via these hypotheses facilitated the development of parsimonious predictive models that targeted the processes and patterns of interest.

[6] This research focused on the interaction of hydrologic, nutrient, and pesticide dynamics at multiple spatial scales (drainage areas spanning 10^2 – 10^4 km²) in the Mississippi-Atchafalaya River Basin (MARB). Sites from the Midwest were complemented with other agricultural drainage basins, primarily the Baltic Sea Drainage Basin (BSDB), and with small watersheds (10^0 – 10^1 km²) representing a variety of land uses, drawn from long term ecological research (LTER) sites and U. S. Forest Service experimental forests [Basu *et al.*, 2010b; Thompson *et al.*, 2011].

[7] A summary of the major findings of the research conducted as a part of the Synthesis Project (papers in the current issue) is presented in section 2, while a schematic of the scales investigated is presented in Figure 1. The research points toward an emerging picture of hydrological and biogeochemical functioning of intensively managed systems, and serves as a point of departure for future research (presented in section 3). Finally, a broad framework targeting a theory of human-catchment interactions is presented in section 4.

2. Synthesis Outcomes: The Emerging Picture

2.1. Hydrological Functioning of Managed Catchments

[8] Conceptually, the hydrological responses of any catchment can be viewed as the filtering of rainfall by the landscape and river network to produce streamflow responses, typically base flow punctuated by episodes of high flow [Dooge, 1959; Nash, 1957]. In Midwestern sites, the components of the hydrological filter are: (1) the vadose zone; (2) the saturated soil zone and its connections to the stream through artificial drainage or subsurface discharge; and (3) the stream network. As depicted in Figure 2, these zones can act as filters in series (e.g., vadose zone to subsurface zone to streams, as in the case of infiltration and drainage) or in parallel, so that a proportion of the flow bypasses some of the filter (e.g., overland flow bypassing the vadose and subsurface zones). Different components of the hydrological filter create variability in stream discharge on different time-scales, which can be observed in the power spectrum of streamflow [Milly and Wetherald, 2002; Dolgonosov *et al.*, 2008]. Different scaling regimes appear to characterize the spectra of Midwestern stream flows: (1) rapid but intermittent movement through surface and subsurface and river drainage networks; (2) slower modulations associated with fluctuations in the water table; and (3) seasonal variation attributable to climatic controls on vadose zone storage [Guan *et al.*, 2011] (Figure 3a).

[9] The properties and behavior of each of the components of the hydrological filter are determined by: (1) the vegetation cover which imposes evapotranspiration losses from the vadose zone, and controls available soil water storage; (2) the maximum size of the soil storage, which is determined by the soil hydrologic properties and depth to the confining layer; and (3) the rate of water movement through the catchment, determined by soils and geomorphic properties and characterized by the inverse of the

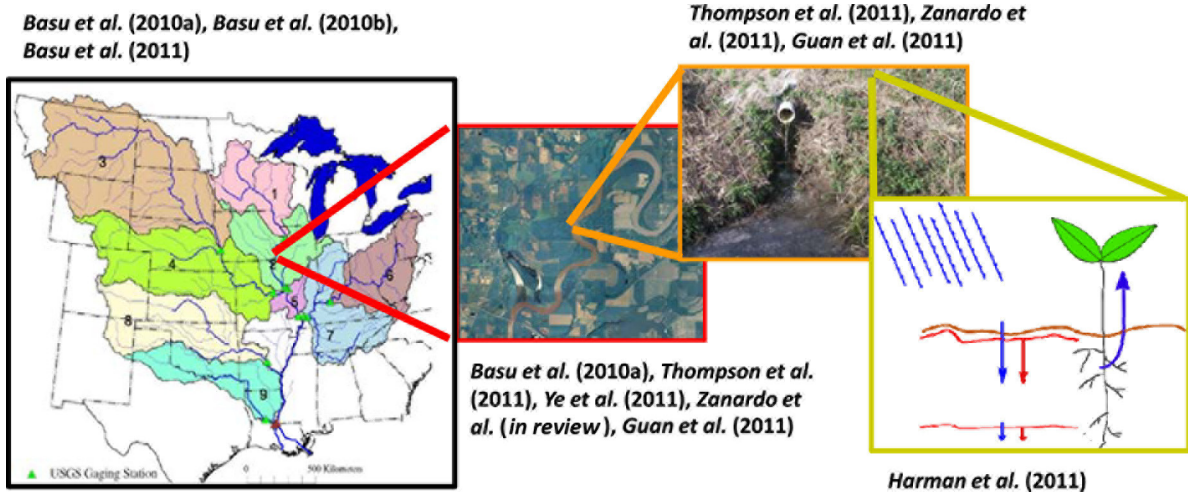


Figure 1. The research discussed in this paper considered a range of scales. The largest basins considered were sub-basins of the Mississippi-Atchafalaya River Basin, with drainage areas of 10^4 km². A range of studies considered mid-sized watersheds with drainage areas on the order of 10^2 km². The smallest drainage areas studied were individual tiles or first-order watersheds of <1 km², while model development started from the point scale (1-D models), and incorporated hillslope, watershed, and river-network processes.

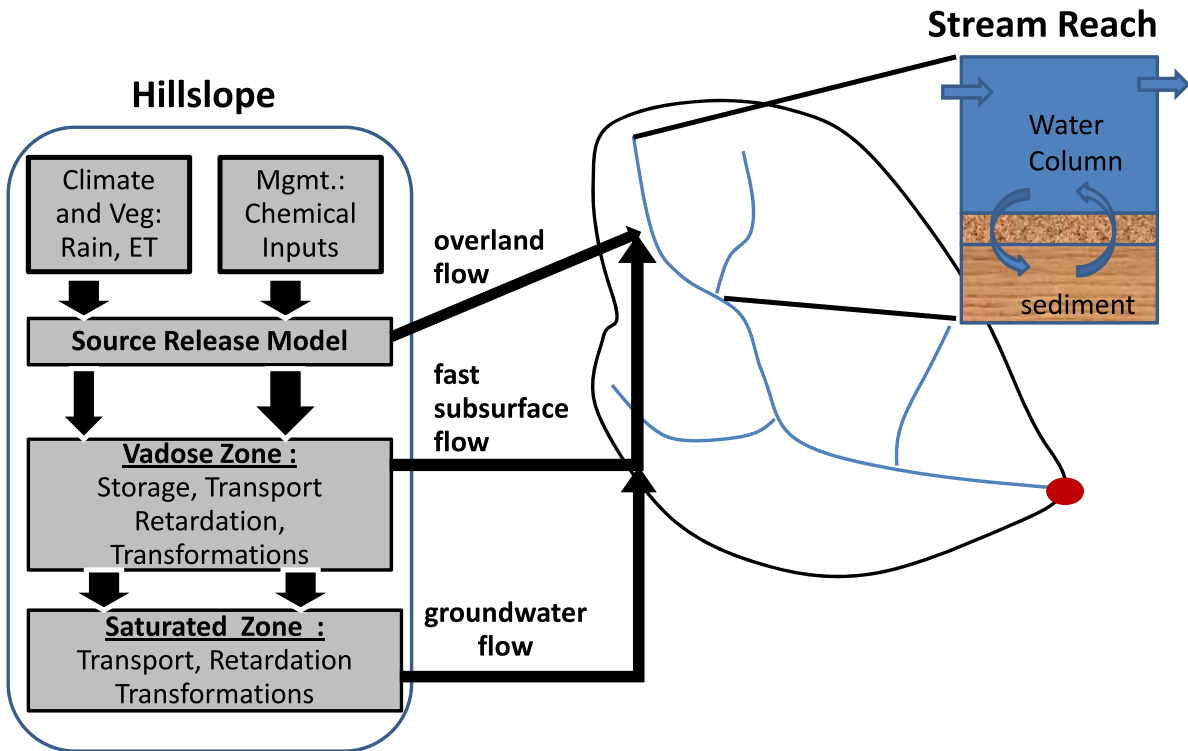
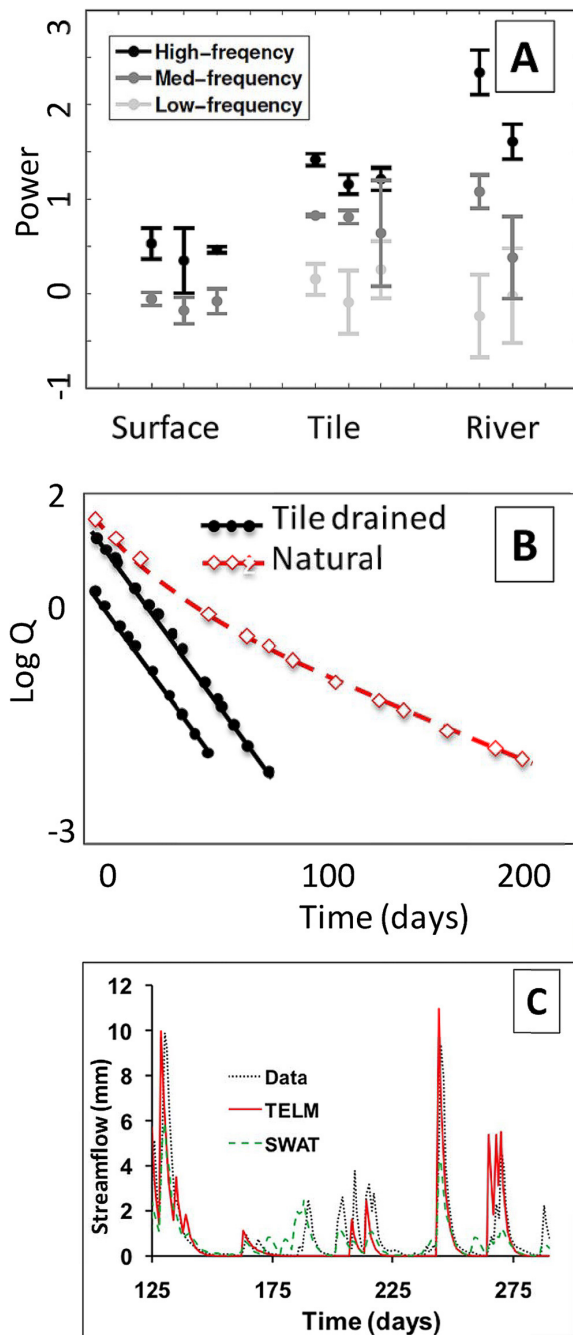


Figure 2. Conceptually the hydrological and biogeochemical functioning of watersheds is related to how the watershed (both hillslope and network) filters incoming signals of rainfall and fertilizer/pesticide application to generate fluxes of water or solutes in streamflow. The hillslope filter includes a source zone, consisting of shallow soils that are relatively enriched by applied agrochemicals, the vadose zone, and the saturated zone. The hillslope is connected to the stream network by overland, tile-, and groundwater flow. The network filter is driven by hydrological attenuation and aggregation, and by biogeochemical processing, mediated by exchange with the channel sediments.

catchment residence time ($k_c[T^{-1}]$). *Basu et al.* [2010a] hypothesized that land management leads to a homogenization of the filter components that has resulted in a more predictable hydrological response in the Midwest. Complex prairie landscapes containing hundreds of plant species have been transformed to monocultural corn-soybean rotations, homogenizing evapotranspiration. Evolution of an extensive network of preferential flow pathways (macropores and vertical cracks) under decades of corn-soy plantings, in conjunction with the engineered drainage tiles and surface ditches, has led to a system that bypasses much of the landscape complexity, delivering runoff rapidly to the stream channels. Tile drains are placed uniformly across the landscape, at a depth of ~ 1 m below the land surface. Consequently, there is less variation in water table elevation

in tile-drained catchments than in natural landscapes, leading to spatially and temporally homogeneous hydrograph recessions. Evidence of this homogenization was found by *Schilling and Helmers* [2008], who observed exponential hydrograph recessions in tiled watersheds, whereas nontiled catchments exhibited power law recessions (Figure 3b). Using agricultural chemicals as tracers of hydrological flow paths, *Guan et al.* [2011] showed the persistence of the signature of tile-drain discharge over multiple spatial scales in the Little Vermillion River watershed (~ 400 km²) in Illinois.

[10] Drawing on this evidence of homogeneity, *Basu et al.* [2010a] proposed that simple water-balance models should be able to capture much of the streamflow response in the Midwest. Using the threshold exceedance Lagrangian model (TELM), they were able to describe the hydrologic responses in Cedar Creek watershed (700 km²) in northeast Indiana [*Basu et al.*, 2010a] (Figure 3c). Subwatershed (~ 10 –50 km²) hydrograph responses were controlled primarily by rainfall and vegetation spatial patterns, with differences in soil playing a minor role. This “functional homogeneity” in hydrologic responses appears to be a strong feature of intensively managed systems in the Midwest. TELM also successfully predicted the hydrograph time series observed in the Little Vermillion River watershed [*Zanardo et al.*, in review]. Other water-balance models that explicitly capture the action of the vegetation, soil, and saturated zone hydrologic filters also reproduce streamflow behavior well: the stochastic model developed by *Botter et al.* [2007a, 2007b] has been successfully employed to describe the probability density function (pdf) of streamflow in study sites (Table 1).



2.2. Biogeochemical Functioning of Modified Catchments

[11] In intensively managed catchments, the biogeochemical inputs of nitrogen (N), phosphorus (P), and pesticides are dominated by agricultural amendments. Mass

Figure 3. Illustrative examples of hydrological behavior in intensively managed catchments. (a) Scaling regimes for discharge in surface drains (three stations), tile drains (three stations), and streams (two stations) in the Little Vermillion River Watershed. The low frequency variations arise from seasonal fluctuations, while the high frequency variations are driven by rapid flow in the drainage and stream networks. The intermediate scaling regime is related to the response of the water table and its connection to the tile discharge, and represents a persistent signal in tile drain and stream discharge across multiple scales (Figure adapted from *Guan et al.* [2011]). (b) Recession behavior (log Q versus time; Q in mm yr⁻¹) in tile drained (two subwatersheds in the Walnut Creek Watershed) and one undrained (natural) watershed (Squaw Creek Watershed) in Iowa. Tile drainage results in an exponential hydrograph response, suggestive of the homogeneity in these dominant flow paths across the watershed. (Figure after *Schilling and Helmers* [2008].) (c) Parsimonious models (in this case TELM) perform as well as distributed models (in this case SWAT) in reproducing hydrological dynamics in the Cedar Creek Watershed, Indiana (Figure adapted from *Basu et al.* [2010a]).

Table 1. Analytical Expressions That Describe Catchment Filtering of Water and Solute as Functions of Hydrologic, Biogeochemical, and Geomorphic Controls

Process	Probability Density Function	Reference and Parameters
Discharge, Q (precipitation filtering)	Mean $\mu_Q = \frac{\lambda}{\gamma k_c}$; Variance $\sigma_Q^2 = \frac{\lambda}{\gamma^2 k_c}$ Mean and variance in Q	<i>Botter et al.</i> [2007a, 2007b] k_c [T^{-1}] = inverse of mean catchment residence time, λ [T^{-1}] and γ [T/L^3] are the mean runoff frequency and mean runoff depth = f (mean rainfall frequency λ_p [T^{-1}], mean rainfall depth γ_p [L/L], vegetation and soil properties)
Vadose zone solute delivery ratio, DR	$p(DR_{vs}) = \tilde{F}\left(2, -\frac{R\gamma_e}{k_d/\lambda_e} \log(DR_{vs})\right) \frac{R\gamma_e}{k_d/\lambda_e} e^{-R\gamma_e DR \frac{1}{k_d/\lambda_e} - 1}$ Mean and variance in delivery ratio $\mu_{DR_{vs}} = \exp\left(-\frac{R\gamma_e k_d}{\lambda_e + k_d}\right)$ $\sigma^2_{DR_{vs}} = \exp\left(-\frac{2R\gamma_e k_d}{\lambda_e + 2k_d}\right) - \exp\left(-\frac{2R\gamma_e k_d}{\lambda_e + k_d}\right)$	<i>Harman et al.</i> [2011] R = retardation coefficient, k_d [T^{-1}] = degradation rate constant in vadose zone, λ_e and γ_e are functions of λ_p and γ_p , is the regularized confluent hypergeometric function
In-stream delivery ratio	$p(DR_{st}) = \frac{\gamma^{\lambda/k_c} \left(\frac{-Lv_f a}{\log[DR_{st}]}\right)^{\frac{k_c - \lambda}{k_c(b-1)}} \exp\left(-\gamma \left(\frac{-Lv_f a}{\log[DR_{st}]}\right)^{\frac{1}{1-b}}\right)}{\Gamma(\lambda/k_c)}$ Note closed form solutions do not exist for mean and variance in DR_{st}	<i>this paper</i> L = length of stream reach, a and b are stream geomorphic parameters linking stream stage h (m) and discharge Q ; $h = aQ^b$; $v_f(L/T)$ = uptake velocity in stream reach; $\Gamma(x)$ is the complete gamma function of argument x , c = normalizing constant, [<i>Abramowitz and Stegun, 1972</i>].

exports of nitrogen and phosphorus are dominated first by crop harvesting and removal, with residual mass exported in the streams or stored in soils [see, for example, *David et al., 2010; Goolsby et al., 1999*]. Pesticides are deliberately designed to have short half-lives in natural systems, and on average ~1% of the applied mass are exported in streams over a broad range of spatial scales in the Mississippi River Basin [*Capel et al., 2001; Wauchope et al., 1992*].

[12] The patterns of nutrient and pesticide export in agriculture-dominated, intensively managed systems can be partitioned between two extreme modes of behavior: (1) chemostatic export in which concentration varies less with flow, exhibited by nitrogen; and (2) episodic export which arises in intermittent pulses with large variability in concentration, exhibited by pesticides (e.g., atrazine). Note that by chemostatic we do not imply that concentrations do not vary on a daily or subdaily timescale. As noted by several researchers [*Kalita et al., 2006; Royer et al., 2004, 2006; Vanni et al., 2001*] concentrations can vary during an event. However, the variations are constrained for chemostatic solutes such that the annual flow-averaged concentration $\langle C_f \rangle$ (= annual export/annual discharge) does not vary significantly from year to year (Figure 4a). Significant interannual variability in $\langle C_f \rangle$ is, however, characteristic of episodic export (Figure 4b). Chemostatic behavior leads to a strong positive linear correlation between annual exported solute load and stream discharge, while episodic behavior lowers such correlations [*Basu et al., 2010b; Thompson et al., 2011*].

[13] As disparate as these modes of export appear to be, a consistent underlying model can be proposed in which

both forms of behavior emerge as a function of chemical reaction rate constants. This model can be visualized as a mass balance for water and solutes across the shallow saturated zone of a tile-drained agricultural field, which is modeled as a well-mixed reactor. For computing water mass balance, the saturated zone is assumed to act as a simple linear reservoir, a reasonable assumption in tile-drained areas as demonstrated by the exponential nature of recession flows [*Schilling and Helmers, 2008*]. Solute mass balance consists of stochastic mass inputs from vadose-zone recharge, mass degradation within the reactor, and persistent linear mass release from otherwise chemically recalcitrant forms of the solute (examples of such recalcitrant forms include sorbed P, or pesticides, or organic N). Running this model generates episodic behavior when the rate of degradation is very high or very low compared to the rate of mass input from storage; but when degradation rates are comparable to rates of mass input, chemostatic export dynamics result (as illustrated in the work of *Thompson et al. [2011]*).

[14] The observed differences between nitrogen and pesticide export patterns can be interpreted in light of these model results. Large stocks of organic N can build up after many years of agricultural management [*Addiscott, 1996; Addiscott et al., 1991; Haag and Kaupenjohann, 2001*], providing a legacy source, which is slowly released back into the mobile phase. The removal (i.e., denitrification) rate of N from the mobile domain is balanced by inputs from the organic store (i.e., mineralization) and fertilizer additions. N is therefore likely to meet the criteria for generating chemostatic mass exports. Conceptually, variations in N concentration in the saturated zone are buffered by a

combination of release and degradation processes that push the concentration to an equilibrium condition. Export of N occurs whenever runoff is generated, and concentrations are relatively consistent between events.

[15] By contrast, degradation rates of pesticides are rather high [e.g., half-life ~60 d for atrazine [Capel et al., 2001;

Wauchope et al., 1992]], precluding their accumulation in the subsurface over long time periods. The pesticides persist in the top few centimeters of the soil surface for ~3–4 months after initial application, during which period rain events create episodic pulses to the surface and groundwater. Because of large degradation losses, the mass leached decreases with increasing time after application [McGrath, 2007], with export ceasing after 3–4 months. The rate of mass input into the system is therefore low by comparison to the rate of degradation (at least when the system behavior is considered over annual timescales), leading to episodic export. Large export events are observed when pesticide application is accompanied by a large rainfall pulse, generating high concentrations in the streamflow [e.g., Klavivko et al., 1991]. This process of intermittent exports being generated only due to a confluence of application and intense rainfall has also been demonstrated with mechanistic models which resolve the dynamics of individual wetting and concentration fronts within the soil [Harman et al., 2011; McGrath, 2007].

[16] In contrast to the observed export patterns of nitrogen, the export of phosphorus (P) displayed scale-dependence. Phosphorus exports were episodic at smaller spatial scales (<200 km²) [Thompson et al., 2011], but chemostatic in large basins in the Mississippi and Baltic Sea [Basu et al., 2010b; Thompson et al., 2011]. The difference in phosphorus and nitrogen export patterns arises from the very different biogeochemistry of the two solutes. Nitrogen is primarily transported in the dissolved phase as nitrate, while phosphorus is transported both in the dissolved as well as the sorbed phase (sediment-bound). The export pattern of P is thus strongly correlated to sediment transport dynamics, possibly leading to the observed scale dependence. Inconsistencies in P export patterns across scales might also arise from point sources of P that becomes more dominant at

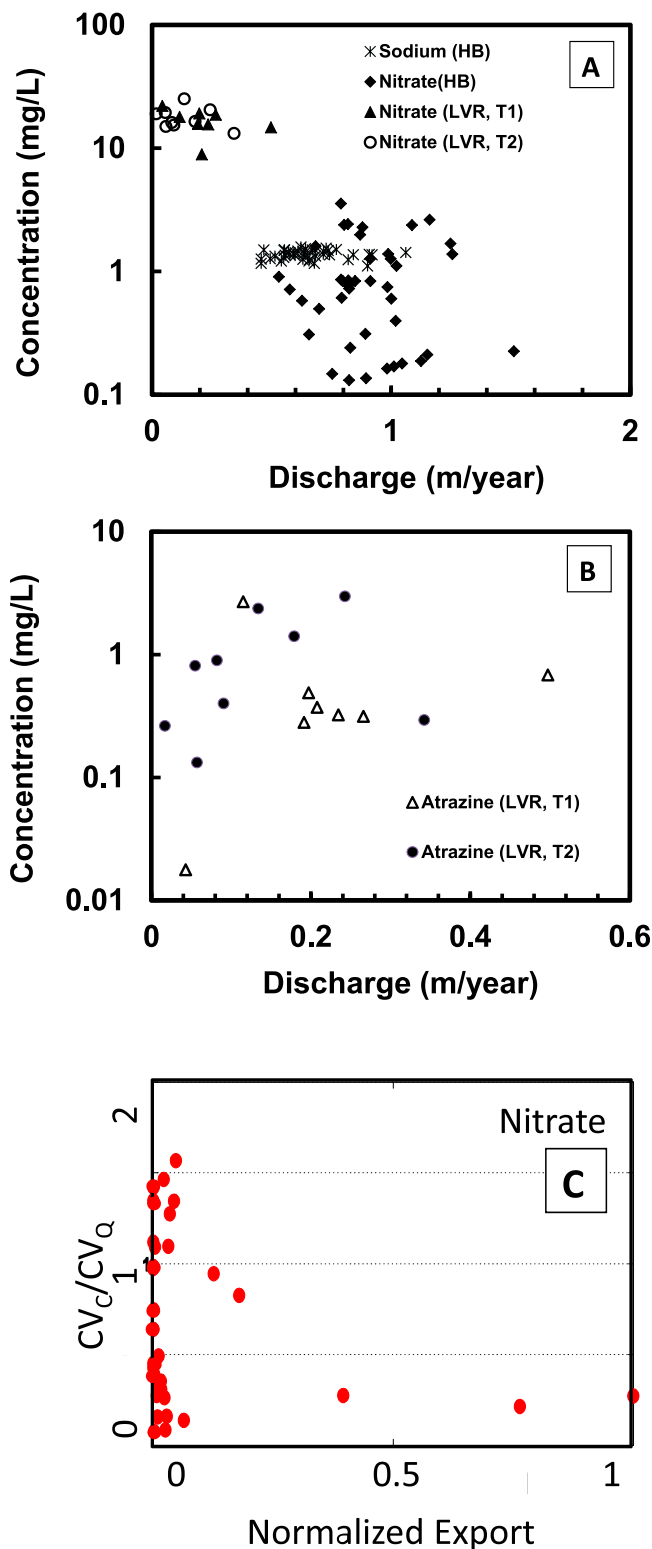


Figure 4. Illustrative examples of biogeochemical behavior in intensively managed catchments based on measured data. (a) Annual flow-averaged concentration $\langle C_f \rangle$ of nitrate as a function of annual discharge from two tile-drained fields in the Little Vermillion River (LVR) basin in Illinois (T1 = 4.8 ha and T2 = 3.3 ha) and a small forested basin in Hubbard Brook (HB), New Hampshire (13.3 ha). Low interannual variability in $\langle C_f \rangle$ in agricultural fields is characteristic of chemostatic behavior, while large interannual variability in $\langle C_f \rangle$ in the forested basin is characteristic of episodic response. $\langle C_f \rangle$ of geogenic solute is provided as a reference. (b) The large interannual variability in $\langle C_f \rangle$ of atrazine characteristic of episodic response. (c) Trends in the coefficient of variation in concentration (CV_C) expressed as a function of the coefficient of variation in discharge (CV_Q) along a gradient in mean annual exported nitrate, taken as a metric of human impact. The annual exported load of nitrate measured at the watershed outlet is normalized by the maximum annual load among the watersheds presented in this figure. Pristine systems behave episodically (high variability in CV_C/CV_Q ratio) while more impacted systems display chemostatic behavior (low variability in CV_C/CV_Q ratio). (Figure adapted from Thompson et al. [2011].)

larger scales [McDaniel *et al.*, 2009]. Further research is needed, however, to understand the observed scale dependence of P export. Spectral and wavelet analysis of time series data sets for flow and solute showed that discharge and nitrate power spectra were similar, while phosphate and atrazine herbicide spectra diverged from that of discharge [Guan *et al.*, 2011].

[17] While the preceding discussion has focused on nutrients and pesticides in Midwestern catchments, the proposed hypothesis can also explain the differences in export that emerge for different solute species, and across the gradient of increasing human impact [Basu *et al.*, 2010b; Thompson *et al.*, 2011]. Concentrations of solutes produced by mineral weathering (such as Ca, Mg, Na, and Si) were found to vary by factors of 3 to 20, while discharge varied by several orders of magnitude in 59 catchments from the U.S. Geologic Survey's Hydrologic Benchmark Network (HBN) [Godsey *et al.*, 2009]. This relatively limited variability in concentration compared to discharge was termed as chemostatic behavior by Godsey *et al.* [2009]. Their observation is consistent with a large, ubiquitous source mass within the system (i.e., the geological parent material), and solute production (because of weathering), and mobilization that is directly proportional to water fluxes. For N in managed Midwestern watersheds, such stores have been created from long-term fertilization [Addiscott, 1996; Addiscott *et al.*, 1991], and can be thought of as the "biogeochemical legacy" of human management. By contrast, there are many examples of nitrogen-limited pristine watersheds in which no nitrogen legacy stores are present [Basu *et al.*, 2010b; Thompson *et al.*, 2011]. In these systems, fluctuations in the concentration of the pore water are strongly dependent on variations in biological nutrient cycling or exogenous input dynamics, leading to episodic export. An example is the Hubbard Brook Experimental Watershed in New Hampshire that exhibits significantly greater variability in $\langle C_f \rangle$, and a lack of correlation between load and discharge compared to the agricultural catchments (Figure 4a). A comprehensive study involving data from pristine and managed catchments [Thompson *et al.*, 2011] revealed that the variability in concentrations in biogenic solutes like nitrate decreased with increasing human impact (Figure 4c). Here, variability is quantified as the ratio in the coefficient of variation in the concentration time series CV_C relative to the coefficient of variation in the discharge time series CV_Q , while human impact is quantified by the mean annual exported nitrate. With increasing human impact, the export mode transitioned from episodic (high variability in CV_C/ CV_Q) to chemostatic (low variability in CV_C/ CV_Q) (see Figure 4c).

[18] The foregoing analysis suggests that a coherent theory can be proposed to explain the emergence of episodic versus chemostatic export: namely, the distinction between source- and transport-limited biogeochemical export. Under transport-limited scenarios, we envisage the presence of a ubiquitous and large chemical source within the catchment that buffers variability in runoff concentration; a situation exemplified by nutrients in agricultural systems and geological weathering products everywhere. The rate of solute mobilization from the source is directly proportional to the water flux, resulting in a low variability in the concentration exiting the landscape. Source-limited cases imply that

there is limited mass available for mobilization in runoff, as observed for nutrients in many pristine catchments and pesticides in agricultural environments. The rate of mobilization depends not only on the water flux, but also on the source mass available in the system which for atrazine has been noted to decrease significantly after the first few storms post-application [e.g., Klavivko *et al.*, 1991]. Source limitation prevails for low rates of mobilization or high rates of depletion (as per the model above), and transitions between source limitation and transport limitation should cause biogeochemical responses to shift from episodic to chemostatic. Preliminary evidence supporting such a shift is presented by Thompson *et al.* [2011] for sites spanning a human-impact gradient, and provide initial empirical evidence supporting a transition from episodic to chemostatic export (Figure 4c).

2.3. Up-Scaling and Prediction

[19] The two modes of export dynamics (episodic and chemostatic) suggest that different controls can be targeted when developing predictive models. Stochasticity of rainfall, solute application timing, and magnitude of solute inputs are the critical controls on episodic export. In contrast, understanding the controls on mean annual flow-averaged concentration $\langle C_f \rangle$ is the key challenge in predicting exports when solutes behave chemostatically. $\langle C_f \rangle$ is expected to vary as a function of management, climate, biogeochemical rate constants, hydrological transport controls, and spatial scale.

[20] To quantitatively explore these issues three different predictive models were developed, each targeting different components of the landscape and different spatial scales as follows: (a) vadose zone scale (HEIST) [Harman *et al.*, 2011]; (b) hillslope scale (SF-MRF) [Zanardo *et al.*, in review]; (c) single stream reach [Botter *et al.*, 2010] and across a stream network [Basu *et al.*, 2011; Ye *et al.*, in review]. These models are described briefly below.

2.3.1. Vadose Zone Scale

[21] The hydrologic event-based infiltration and solute transport model (HEIST) is a 1-D vertical model that translates inputs of reactive solutes (i.e., fertilization or pesticide application) and water (i.e., rainfall) to the vadose zone to a stochastic delivery of water and solute mass to the water table. HEIST accounts for hydrological and biogeochemical interactions within the vadose zone by explicitly simulating evapotranspiration (ET), retardation, and degradation [Harman *et al.*, 2011]. The episodicity of solute delivery, as described by the clustering of solute leaching events, increased in drier climates (with higher ET), and with larger retardation and degradation losses. The simplicity of the HEIST conceptualization enabled the development of analytical and semianalytical expressions for pdfs of solute delivery ratio using existing theory of stochastic soil water dynamics (see Table 1). These pdfs can be used to explore how alterations in the stochasticity of rainfall and land-use shifts would impact groundwater vulnerability to leaching from episodic solute export from the vadose zone.

2.3.2. Hillslope Scale

[22] HEIST is a point-scale model focused on vadose-zone processes, and can be used for groundwater vulnerability studies. It is specific for episodic solutes with no legacy sources in the landscape. In contrast, the mass

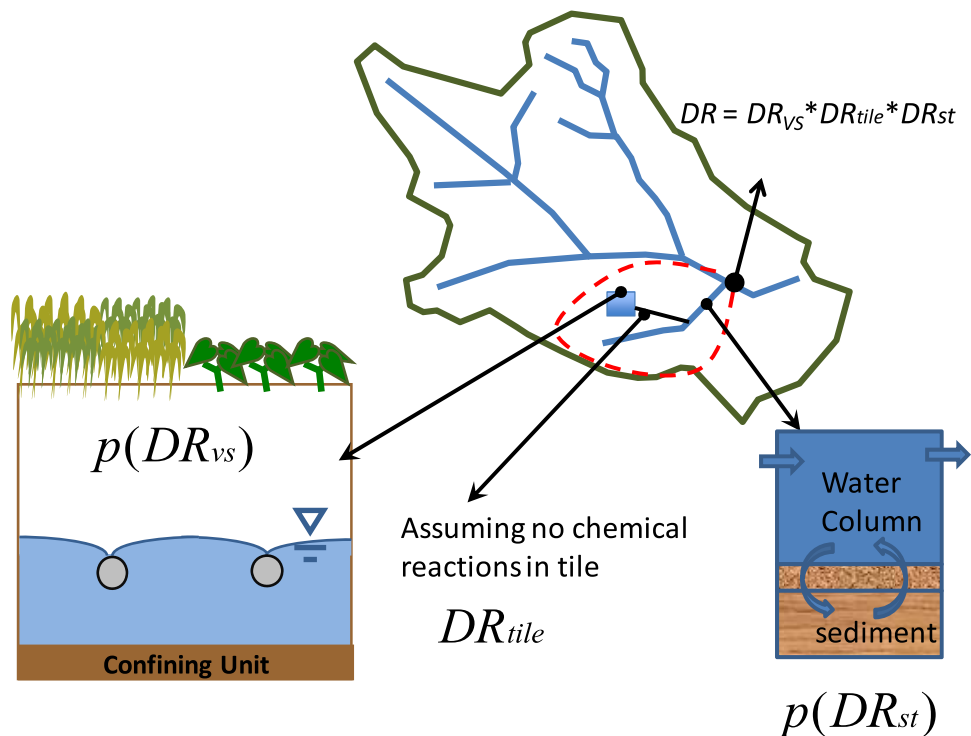


Figure 5. Illustrative example demonstrating the use of the filters in series concept to develop expression for the pdf of solute delivery ratio at the outlet of a first order catchment as a function of the pdfs of the delivery ratio in the vadose zone, tile drain, and stream reach (see Table 1 for the analytical expressions).

response function (MRF) approach, developed by *Rinaldo and Marani*. [1987], is a parsimonious model based on travel time distributions at the watershed scale. The MRF model can be used for legacy solutes like nitrogen. MRF was generalized by adding a source function (SF) module that describes pesticide release from a narrow zone near the soil surface, and linked to TELM to capture the complex biogeochemistry of pesticides [*Zanardo et al.*, in review]. The coupled SF-MRF model was able to describe pesticide export dynamics at multiple spatial scales with minimal calibration. SF-MRF can be used to examine episodic or legacy solutes at intermediate spatial scales, offering a tool to explore the relative effect of internal and external sources on the shifting of solute export from chemostatic to episodic.

2.3.3. Stream Network

[23] HEIST and SF-MRF are primarily focused on hill-slope processes that dominate biogeochemical export in lower order watersheds, and especially for solutes like atrazine that undergo minimal in-stream degradation. As watersheds become larger, the importance of aggregation and attenuation along the river network increases, and models must capture in-channel processes. The inverse relationship between the in-stream removal rate constant, k [T^{-1}], and the stream stage, h [L], ($k = v_f/h$) was used to develop the pdf of k as a function of hydrology, driven by stochastic fluctuations in the stream stage, h , and biogeochemistry, as manifested in the solute uptake velocity, v_f [*Botter et al.*, 2010]. In this paper, we extended their formulation to develop the pdf of the in-stream delivery ratio $DR (= \exp[-k\tau]$; $\tau =$ residence time [T]) (see Table 1). These simple analytical

models enable the exploration of the effects of uncertainties in climate, hydrologic, and biogeochemical parameters on solute delivery ratio within a stream reach. Model results indicated that the solute removal efficiency ($1 - DR$) increases with discharge variability (quantified as the coefficient of variation of the streamflow distribution) [*Basu et al.*, 2011]. For a gamma distributed streamflow pdf, increase in variability leads to a distribution with greater proportion of smaller streamflow values [*Basu et al.*, 2011], thus increasing the efficiency of solute removal based on the relationships presented above. While simple analytical stochastic modeling is possible at the reach scale, aggregation along the stream network requires numerical modeling [*Basu et al.*, 2011]. A new stream network model was developed to mechanistically describe nitrogen transformations by adding biogeochemical components to the existing representative elementary watershed (REW) model proposed by *Reggiani and coauthors* [*Ye et al.*, in review; *Reggiani and Schellekens*, 2003; *Reggiani and Rientjes*, 2005]. Model results indicated that the functional form of the inverse stage-dependence of k was independent of spatial and temporal averaging at scales as large as the Mississippi Basin [*Basu et al.*, 2011]. The consistency with which the relationship scales up is promising and indicates that it might be possible to estimate in-stream nutrient removal without spatially distributed network analysis. Indeed, the pdf of the spatio-temporally averaged rate constants at the scale of the Mississippi Basin was described adequately using the reach scale analytical model developed by *Botter et al.* [2010]. Stochastic analytical modeling also indicated that such scale invariance is characteristic of humid

domains, while strong nonlinearities and scale dependence arise in arid systems [Basu *et al.*, 2011].

[24] The models described above demonstrate that understanding the dominant controls on solute export in managed catchments enables the development of parsimonious, process-based models. This allows the development of several analytical functions that describe the pdfs of delivery ratios in different components of the landscape (see Table 1). Such functions explicitly link the uncertainties in predicting landscape responses to the stochasticity of the climatic, hydrologic, and biogeochemical controls, and enable the description of uncertainties without explicit Monte Carlo type analysis. As an example, if we assume three components of the hydrologic/biogeochemical filter connected in series: vadose zone, tile drain, and stream reach, the solute delivery ratio of the combined system can be expressed as the product of the delivery ratios of the individual components (see Figure 5). Thus, the efficiency of solute delivery can be expressed as a function of the stochastic climatic controls, landscape hydrologic filters and biogeochemical controls, and geomorphic and biogeochemical attributes of the stream. To extend this idea further, the delivery ratio at any node in a stream network can be expressed as a function of the delivery ratios along the many pathways that lead to that node (filter components in parallel). Uncertainties specific to each of the components of the filter can then be propagated to estimate the uncertainty in the delivery ratios. This approach provides an alternative framework for catchment-scale solute transport modeling.

2.4. Outstanding Issues

[25] The synthesis project work has now reached the stage where multiple predictive models have been developed to describe hydrological and biogeochemical export dynamics in managed catchments. Simultaneously, the project team has gathered data sets describing time series of hydrographs and chemographs from a diversity of catchments globally, spanning over seven orders of magnitude in spatial scale. Although model development proceeded with an awareness of these data sets and the hypothesized underlying dynamics that dictate the patterns in export, the full potential of combining the models, data, and hypotheses have not yet been fully explored. The next stage of model development is a comprehensive validation of these tools against available data for all solutes other than nutrients and pesticides, which have been considered to date. Example questions that will guide this exploration include:

[26] 1. Can the models reproduce multiple signatures of hydrological and biogeochemical export (i.e., not only time series and export magnitudes, but the frequency domain characteristics explored by Guan *et al.* [2011])?

[27] 2. As more data from diverse catchments along the gradient of human impacts are compiled, do models support the hypothesized transition from chemostatic to episodic modes of export as rate parameters are altered?

[28] In some cases, the models and hypotheses developed may prove difficult to validate without new campaigns of data collection and analysis. For instance, the evolution of biogeochemical reactions and rates over multiple timescales, the magnitudes of legacy stores and their nature, and the growth or depletion of such stores is largely unknown. Quantification of these processes and catchment states requires

measuring over large spatial and temporal scales, posing a significant logistic challenge. Similar challenges apply to evaluating predictions of reaction rate scaling across large spatial scales in river networks. Given the challenges of observational studies across scales, intermodel comparisons between the simple hypotheses and approaches developed here, and more complex, distributed hydrological and biogeochemical models might offer an appropriate way forward.

3. Future Work

[29] Our synthesis research documented above, highlights a number of emerging research themes (discussed below) which may set the stage for future advances in catchment science that address the coupling between hydrologic and biogeochemical processes at multiple scales and over varying human impact gradients.

3.1. Catchment Biogeochemical Classification: Spatial Variation

[30] The results presented above suggested that, at least for the case of nitrogen (and for phosphorus in large catchments), the annual exported load can be predicted with knowledge only of the hydrologic variability, and a watershed-specific but stationary (time-invariant) mean, annual, flow-weighted concentration, $\langle C_f \rangle$. At present, however, $\langle C_f \rangle$ must be empirically determined. Several studies point to linear relationships between various measures of human impacts (e.g., percent cropland, percent forested area, population increase, and fertilizer inputs) and exported nutrient loads (e.g., nitrogen, phosphorus, and inorganic and organic carbon) [Barnes and Raymond, 2009; David and Gentry, 2000; Goolsby *et al.*, 1999]. Understanding the controls on $\langle C_f \rangle$ would allow variations in agricultural management (e.g., percent cropland, fertilization practices, and crop yield) and biophysical properties (e.g., soil organic content and rate constants) to be incorporated in predictive models. If the effects of anthropogenic factors could be accounted for, then the underlying variations in $\langle C_f \rangle$ would enable the classification of catchments as a function of their intrinsic biogeochemical processing abilities. Appropriate research methodologies to address the variation in $\langle C_f \rangle$ include further data analysis, modeling, and targeted isotope studies in representative systems to adequately quantify the partitioning of carbon and nutrients in different compartments of an agricultural ecosystem.

3.2. Catchment Trajectories: Temporal Variation

[31] Cross-catchment comparisons of pristine and managed catchments indicate that controls on solute export shift from biogeochemical to hydrologic along the gradient of human impacts. However, the details of how these catchment trajectories have evolved in response to nonstationary anthropogenic forcing, and what roles nonlinearity in responses and multiple thresholds play in the trajectories of increasing human impact are yet to be evaluated and modeled. An important research question is whether the past can be reconstructed to estimate the magnitude of the legacy stores of nutrients, and how these stores have built up over time. Also of interest are the reverse trajectories (impacted to pristine) that come into focus especially during restoration activities. The time- and space scales on which changes in land use are reflected in hydrological and water quality

change must be understood to assist in efficient land-use planning and to evaluate proposed restoration options. These scaling properties and their dependence on landscape attributes are poorly understood, in part due to the significant resource demands of field monitoring over large time- and space scales. Available studies (e.g., on N release from fallow land at the end of several decades of N fertilization [Addiscott, 1996; Addiscott *et al.*, 1991]) suggest that temporal lags on the order of decades may apply even at the scale of a single field [Meals *et al.*, 2010; Tomer and Burkart, 2003]. Targeted monitoring, supported by detailed modeling studies, is needed to determine these timescales.

3.3. In-stream Processes

[32] Theoretical progress has been made primarily in understanding the in-stream dynamics of dissolved solutes, particularly nitrate. There are two obvious avenues for extending this theory: (1) examining particulate-bound contaminants, and (2) considering passive transport of living organisms. Sorbed contaminants (e.g., phosphorus species, heavy metals, pesticides, and endocrine disrupting chemicals) are primarily transported on dissolved organic carbon and colloidal or very fine fractions of suspended solids. Important living organisms, including pathogens (e.g., *E. coli*), pests (e.g., *Didymosphenia geminata*), or larvae of invasive species (e.g., zebra mussels) undergo passive transport in rivers. The growth of these species depends on their local in-stream environment (e.g., availability of carbon and nitrate, stage variations, etc.), as well as their adhesion to suspended solids or bottom sediments. Linking population biology approaches to variability of the in-stream environments and propagation within a network offers an important avenue for future theoretical development [Righetto *et al.*, 2011].

[33] While theoretical developments are possible, the limited availability of large-scale stream biogeochemistry data severely limits our ability to test the hypotheses generated by these theories. Several theoretical predictions, such as observed (based on stream network models) *k-h* scaling behavior, and the dependence of in-stream processing on hydro-climatic drivers [Basu *et al.*, 2011] are well suited for empirical testing with long-term watershed-scale data. Such testing is a critical next step in understanding the scaling of biogeochemical processing in stream networks.

3.4. Integration With Socio-Economic Factors

[34] The studies described here focused primarily on biophysical controls of catchment hydrology and biogeochemistry, assuming that the management actions undertaken could be treated as fixed and exogenous. In reality, management changes over time in response to a complex array of economic, social, and environmental drivers. Understanding the feedbacks between environmental systems and management strategies is required to: (1) enable robust predictions of hydrology and biogeochemistry (e.g., under scenarios of land use or climatic changes), and (2) to provide support to decision-makers. The first target addresses primarily the development of a science of integrated human and natural systems, an outcome that is of increasing value given the magnitude of the human footprint on Earth's ecosystems. The second target recognizes that considerable financial and social investments, particularly in terms of food and energy production, are associated with the current status of

intensively managed catchments, and that environmental improvement will require valuation of ecosystem services and some optimization of tradeoffs between these services and existing land-use values. Both outcomes depend on integrating the emerging picture of hydrology and biogeochemistry in intensively managed systems into a coupled social-environmental framework that can address feedbacks and trade-offs explicitly.

4. Conclusions

[35] Intensively managed catchments provide an excellent set of case studies for studying the interconnections between human activity and catchment function as manifested in hydrological and biogeochemical change. The results emerging from our synthesis work discussed above suggest a broad hypothesis: Human modifications overwhelm local biophysical and structural heterogeneities, transforming complex natural systems into more homogeneous, engineered, and predictable systems.

[36] Cadenasso *et al.* [2006] suggested that complexity in landscapes or ecosystems can be thought of as having three dimensions: (1) complexity in structure, meaning heterogeneity in soil type, vegetation, and topography; (2) complexity in architecture, meaning heterogeneity in transport pathways or connectivity; and (3) complexity in contingencies, meaning a broad range of responses of a landscape or catchment to imposed perturbations. The research summarized in section 2 and discussed in detail in papers in this issue suggest that in the Midwest, human modifications have reduced complexity across all three dimensions: structural complexity has been eliminated by monocultural cropping and soil management practices; architectural complexity has been diminished by the extensive network of tile- and ditch-drains; and complexity in landscape biogeochemical response has been diminished by the legacy store of nutrients in the subsurface which buffer interannual variations in biogeochemical processing. The consequences of this reduction in complexity are that hydrological responses in artificially drained agricultural watersheds are controlled primarily by the stochasticity in rainfall, while biogeochemical export of nutrients follows a linear relationship between annual nutrient load and discharge in managed watersheds that is absent in pristine catchments.

[37] It is tempting to speculate that such simplifications in landscape function may prove to be a common outcome of human modifications and management given that increased efficiency and consistency of outputs maximize economic returns in the absence of external costs. Increase in the predictability of responses with management is an intriguing aspect of human-catchment interactions that should be explored further for other kinds of human impact (e.g., urbanization).

[38] An ongoing stimulus for research exists in answering applied questions (for example, how to mitigate ecological impacts of intensive agriculture and land management) in intensively managed systems. This requires the coupling of hydrologic and biogeochemical models with ecological models that quantify impact and socio-economic models that assess the feasibility of alternate management strategies. Predictability of landscape response and the attendant parsimony of hydrologic and biogeochemical models imply

strong potential for effective coupling. Explicitly introducing the socio-economic and ecological drivers into an integrated theory of managed landscapes has the potential to offer new insights into the long-term behavior and trajectories of these systems. This approach could underpin new ways to holistically evaluate agricultural and environmental services in managed landscapes, and ultimately providing a framework for effective management of these important ecosystems.

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