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# Contaminant load-discharge relationships across scales in engineered catchments: Order out of complexity

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**Abstract:** Understanding nutrient dynamics in diverse ecosystems is critical in evaluating ecological impacts (e.g., eutrophication; coastal hypoxia) from increased loads of nitrogen (N), phosphorus (P), and carbon (C), and for evaluating the atmospheric impacts from $N_2O$ produced during denitrification. The linkage between hydrologic and biogeochemical cycles is crucial for predicting nutrient cycling in these ecosystems. Examining the impacts of large-scale human modifications of watersheds (e.g., land-use intensification for food production; hydrologic modification though extensive tile-drainage, etc.) on the hydrologic responses, associated nutrient loads, and ecological impacts at various scales has been the focus of large-scale monitoring and modeling studies over the past two decades.

We hypothesize that human modifications and intensive management of watersheds lead to more predictable hydrologic responses, typical of an engineered, less-complex system rather than natural, complex systems. Engineered structures in modified catchments include regular networks of tile-drains (or sewers) with surface and subsurface inlets, unlined ditches, weirs, etc to promote drainage. In such engineered catchments, simple and efficient predictive models are sufficient to describe the hydrologic and biogeochemical responses across catchment scales. Here, we explore four important questions related to hydrologic predictions and biogeochemical responses observed at diverse temporal scales (from event-specific responses to inter-annual variations) and spatial scales (ranging from $10^1$ to $10^6$ km$^2$): (1) Can event by event hydrographs and chemographs be predicted without model calibration? (2) Can nutrient loads be predicted given only information on discharge, use patterns (sources), and attenuation (losses)? (3) Can the in-stream biogeochemical attenuation rates observed for these nutrients be estimated? (4) How do the intra-annual variations in the rainfall-runoff processes modulate the temporal variations in biogeochemical processes controlling contaminant losses in streams?

We first examined monitoring data available for two watersheds (~700 and 2,000 km$^2$) in Indiana, USA, and developed a simple model (Threshold Exceedance Lagrangian Model, TELM), to predict observed hydrographs and chemographs over a four-year period. TELM predictions, requiring no calibration of model parameters, were in good agreement with the measured hydrographs and chemographs. Un-calibrated TELM predictions were also close to those predicted by a popular, distributed-parameter model, SWAT, whose parameters were calibrated using a training dataset. Next, we examined the relationship between seasonal or annual total discharge ($Q$; $L^3L^{-2}T^{-1}$) and area-normalized annual contaminant loads ($L$; $ML^{-2}T^{-1}$) measured in three watersheds: Cedar Creek (~700 km$^2$) and Wildcat Creek (~400 km$^2$) in Indiana, USA, and Little Vermillion River watershed (~200 km$^2$) in Illinois, USA. In all three watersheds, a linear *L-Q* relationship was noted for nitrate and atrazine. Furthermore, we examined the hydrologic and water-quality monitoring data available for several large sub-basins ($2\times10^5$ to 8x105 km$^2$) the Mississippi River Basin, and found consistent linear *L-Q* relationships. By comparing the load-discharge data for a conservative constituent (bicarbonate) with that for more reactive constituents (DOC, nitrate, *ortho*-phosphate), we identified the relative differences in nutrient attenuation. Finally, we derived explicit analytical expressions for explaining the reported effective rate constants ($k_e$, $T^{-1}$) scale-dependence (or stage-dependence), and for the intra-annual temporal variability in observed denitrification rate constant within streams. It was shown that stream hydrologic fluctuations (i.e., stage) serve as the dominant (first-order) controls on biogeochemical processing of nutrients in the benthic sediments. Random, temporal fluctuations in river stage – resulting from hillslope-climate interactions – result in fluctuations in nutrient attenuation rates and nutrient loads in stream networks.

**Keywords:** *Hydrographs, Chemographs, Nutrient Loads, Watershed Modeling, Stream Networks, Water Quality, Denitrification, Intra-Seasonal Variability*

## 1. INTRODUCTION

Current research in watershed hydrology is focused on reproducing the hydrologic responses of individual catchments using detailed, process-based, distributed models with large number of parameters that are usually difficult to measure at the required spatial or temporal scales. One common feature of these models has been model calibration using "training" datasets gathered over a restricted timeline, cross-validation using other datasets, and then generating model forecasts for much longer periods. While numerous, creative ways of calibration and optimization have been developed, this approach has two basic limitations: (1) equifinality or non-uniqueness, where multiple combinations of model parameters might produce the same model outcome; and (2) lack of model validation at spatial scales smaller than at which model calibration has been done. In contrast, few studies have recognized the value in studying patterns across catchments with an attempt to classify catchments and identify the dominant drivers of response for each catchment class. This process results in the development of empirical theories based on emergent patterns of catchment response across scales, which are then generalized using theories regarding natural organization and self similarity underlying landscape heterogeneity (e.g., Sivapalan, 2003; Savenije, 2008).

Our objective here is to adopt the latter approach and use the Mississippi River Basin as a case study to demonstrate how 'order' and simplicity can emerge out of complex interactions in space and time. In this river basin, intensive management requiring applications of large amounts of fertilizers, pesticides, and animal manures has contributed to widespread, adverse water-quality impacts (nitrogen, phosphorus, pesticides, pharmaceuticals, hormones, pathogens, etc.) that have major repercussions to water quality at both the local scale (streams, lakes), and as far away as the Gulf of Mexico (e.g., coastal hypoxia). Hydrology of the Midwestern USA has been modified extensively over the past century, as European settlers drained vast tracts of wetlands-lowlands (forests and prairies) to create productive croplands. The landscape was drained using an extensive network of tile-drains and unlined ditches that, along with the existing network of natural preferential flow paths (cracks, root-holes, bio-channels) in the shallow soils, created an effectively high permeability bypass-flow hydrologic system. In addition, vast tracks of land (~75%) in this region are planted to corn-soybean rotation, and the soil/crop management (conservation) practices tend to be quite uniform to achieve maximum grain yields, and to minimize soil losses through sediment runoff. As a result, there is a remarkable emergence of scale-invariance typical of fractal domains, and simplicity to hydrologic processes observed in the watersheds located within this region. At most spatial scales of interest, event hydrographs and chemographs show quick response (time to peak) and rapid recession (few hours to days), with the forcing functions (rainfall and vegetation) being the dominant drivers of hydrologic response.

Based on these observations, our overall hypothesis is that human modification of catchments increases predictability, compresses time scales of response, and decreases the level of system complexity. Thus, simple and efficient modeling might suffice for predicting hydrologic and biogeochemical responses of these engineered watersheds. Here, we examine a parsimonious modeling approach to predict event-specific hydrographs and chemographs in Midwestern USA watersheds, and examine emerging spatio-temporal patterns in contaminant loads observed across the Mississippi River Basin.

## 2. EVENT HYDROGRAPHS AND CHEMOGRAPHS

Based on the overarching hypothesis stated above, our objective was to seek predictions that are robust to provide adequate reproductions of multiple hydrograph and chemograph events within a crop growing season, and utilize few lumped parameters whose values over spatial domains can be readily estimated without calibration to the observed hydrographs. Basu et al. (2009a) recently developed the Threshold Exceedance Lagrangian Modeling (TELM) as an alternate modeling approach, derived from patterns noted in watershed monitoring data, and underpinned by the following principles borrowed from description of ecosystem attributes: (1) loss of hydrologic *complexity* because of extensive landscape modifications (tile-ditch drainage) and uniform crop management practices (corn-soybean rotation); (2) *functional homogeneity* in terms of hydrologic response in spite of spatial, structural variability; (3) *dominance* of a single hydrologic pathway (tile-ditch flow); (4) *thresholds* for triggering flow events (soil-water storage excess); and (5) temporal *persistence* of patterns (recession curves). They examined the utility of this simplified modeling approach using monitoring data from Cedar Creek watershed (~700 $km^2$). This watershed is a part of the St. Joseph River Basin in northeastern Indiana, and drains two 11-digit sub-watersheds the Upper Cedar (HUC 04100003080) and the Lower Cedar (HUC 04100003090). The hydrographs observed at the Cedar Creek Watershed outlet during the entire crop growing season (April-October) could be well-reproduced by the TELM approach. Also, the chemographs measured for the herbicide atrazine could be reproduced by the TELM model (Figure 1). (Basu et al., 2009).

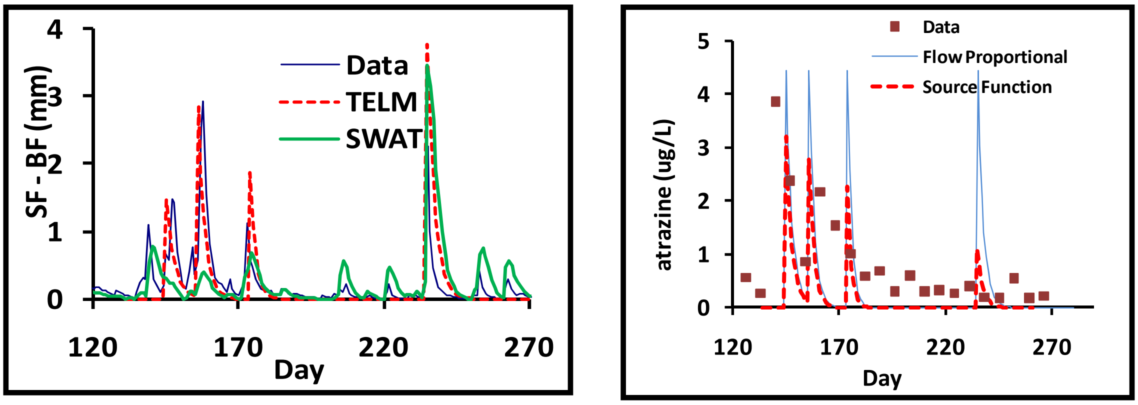


**Figure 1.** Measured and predicted (TELM and SWAT) hydrographs and atrazine chemographs in Cedar Creek Watershed. (Basu et al., 2009)

An important feature of these predictions is that they required no calibration of the TELM model parameters. Given this, the match of hydrographs is impressively similar to the predictions based on a popular distributed parameter model, SWAT, which required calibration of about 28 model parameters (Kumar and Merwade, 2009). Equally satisfactory hydrograph and chemograph predictions could be achieved using TELM in years with "normal" rainfall patterns. However, in years with more extreme variations (e.g., mid-season droughts), the TELM model provided less satisfactory prediction, primarily as a result of failure to: (1) model variations in crop growth during the year; and (2) account for reduction in evapotranspiration losses resulting from soil-water storage deficits during droughts. Further improvements to the TELM model to account for such effects are now being made.

## 3. SEASONAL CONTAMINANT LOADS

It is also of interest to understand how the contaminant loads representing the intra-seasonal patterns in these event hydrographs and chemographs scale up when integrated over the entire crop-growing season. How are the intra-seasonal variations in contaminant loads controlled by the annual variations in rainfall patterns and the resulting stream-flow variations at the watershed scale? We examined available data from several years of monitoring in three agricultural watersheds in the Midwestern USA: (1) Cedar Creek Watershed (CCW) mentioned above, (2) Wildcat Creek Watershed (WCW; ~400 $km^2$), in central Indiana, and (3) Little Vermillion River Watershed (LVRW; ~200 $km^2$), in Illinois. All three watersheds share similar attributes in that they are dominated by cropland (corn-soybean), have similar soils, share a (glacial) geologic history, and are extensively tile-ditch drained. For the LVRW, monitoring data (Kalita et al., 2007) gathered at three locations, representing drainage areas of a single tile drain (6 ha), and two sub-watersheds (69 and 186 $km^2$) are shown. The data for the WCC and CCW are for the herbicide atrazine, while the data for the LVRW are for nitrate.

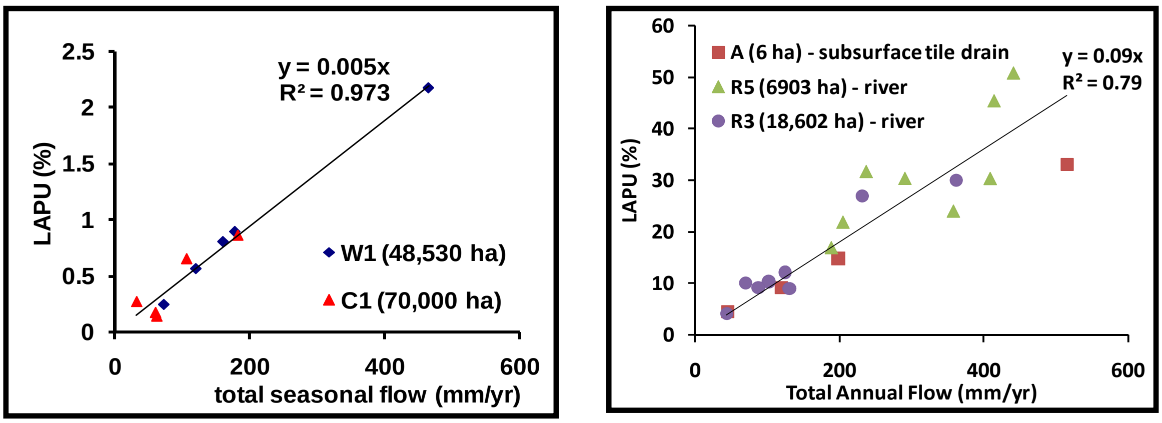


**Figure 2.** Load-discharge relationships based on water-quality monitoring in three Midwestern US watersheds.

In all three watersheds and for multiple seasons, year-to-year variations in stream flow and contaminant loads vary a great deal. But, we observe (Figure 2) a surprisingly consistent, linear relationship between the cumulative (seasonal or annual) stream flow and the cumulative contaminant load when expressed as LAPU or the loss of applied amount as a percent of that applied to the crop fields. That is, low-flow seasons consistently translate to smaller nitrate or atrazine loads, while higher loads are generated during high-flow seasons. The slope of these regression lines represents a seasonal, flow-averaged contaminant concentration, $C_f$ ($ML^{-3}$), and can be used as a hydrologic "signature" of these watersheds, at least under current land-use practices. A single regression line for multi-year data from CCW and WCW suggests that these two watersheds are apparently "functionally similar" in terms atrazine fate and transport. Similarly, multi-year and multi-scale nitrate data for the LVRW suggests that this watershed is functionally homogenous in terms of nitrate fate and transport. Also, superposition of the data for the three spatial scales (6 ha; 6903 ha; and 18,602 ha) suggests that nitrate in-stream processing is quite small. It is also of interest to note that while the LAPU for atrazine is <2.5% in CCW and WCW, nitrate LAPU varies from 10-60%. These patterns are reflective of the differences in the rates of biogeochemical processes that attenuate atrazine and nitrate in the soils and within the streams.

Do these patterns persist over even larger spatial scales? We examined available nitrate monitoring data for nine large sub-basins (200,000 $km^2$ to 800,000 km2) within the Mississippi River Basin to examine load-discharge relationships. These sub-basins have diverse land uses, although agriculture is still dominates (from ~30% to ~80%). In spite of their large size and diversity in soils, geology, rainfall patterns, and land use, once again we find a linear relationship (Figure 3) between the recorded annual cumulative discharge (m/yr) and the measured nitrate load ($g/m^2/yr$), except that now the basins can be grouped by two representative regression lines. Flow-averaged nitrate concentration of 2.5 mg/L and 1.3 mg/L describe the behavior of all nine sub-basins, compared with $C_f$ of about 10 to 30 mg/L observed at the scale of a single tile. Decrease in $C_f$ at larger scales is attributed to differences in both nitrogen application rates and to in-stream reactions (e.g., denitrification, plant uptake, etc.) that remove nitrate from the system. The half-life of nitrate in streams have been reported to vary between 0.1 day to 100 days (Alexander et al., 2000, 2009), while travel time within the Mississippi River Basin is a few weeks. The relative importance of reactive processes at different observation scales needs to be explored further.

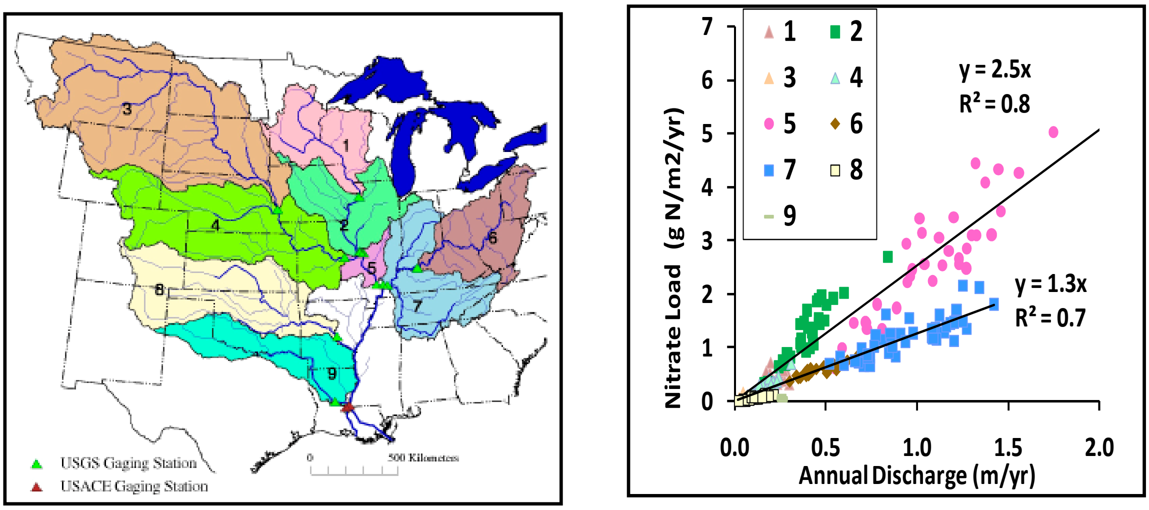


**Figure 3.** Load-discharge relationships based on nitrate monitoring data in eight sub-basins of the Mississippi River Basin.

We next compiled water quality monitoring data from three large sub-basins (Ohio River, Upper Mississippi River, and Missouri River) and examined the patterns in load-discharge relationships for several other dissolved constituents (dissolved inorganic carbon (bicarbonate), DIC; dissolved organic carbon, DOC; *ortho*-phosphate, OP; and total phosphorous, TP). We assumed DIC to act as a conservative tracer, and plotted loads of all other contaminants (for the three sub-basins) as a function of DIC load. This resulted in a collapse of the data for all three sub-basins (indicated by different symbols) to a single line for each of the constituents (Figure 4).

The slope of the line is unique for a contaminant, and is a function of the relative inputs ($M$) of the constituent and DIC, and the effective degradation rate within the system:

$$\text{Slope} = \frac{L_C}{L_{DIC}} = \frac{M_{app,C}}{M_{app,DIC}} \frac{LAPU_C}{LAPU_{DIC}} \qquad [1]$$

where LAPU is, as before, the load expressed as a percent of the use (application rate). Here, $LAPU_{DIC}$ is scale-invariant because DIC does not transform in the system (i.e., acts as a nonreactive tracer), while $LAPU_c$ for the other constituents is a function of the effective degradation rate at the scale of observation. Collapse of the data for three sub-basins to a single line for each constituent indicates that the effective degradation rates at the scale of observation are the same. The scatter of data points about the line is expected to increase with decrease in the scale of observation due to local differences in degradation rates.

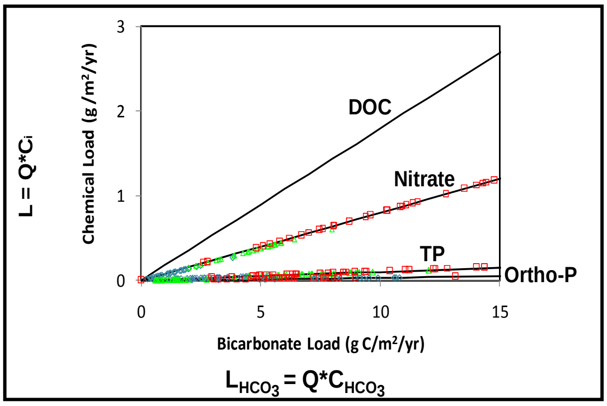


**Figure 4.** Relationship between nutrient (DOC, nitrate, *ortho*-phosphorous, and total phosphorous) loads and bicarbonate loads, based on water quality monitoring in three sub-basins of Mississippi River Basin.

## 4. SPATIAL PATTERNS IN IN-STREAM LOSSES

Nutrient loss mechanisms in streams have been primarily studied over small reaches as nutrient-spike experiments under base-flow conditions (Mulholland et al., 2008), with few studies at larger scales using nutrient mass-balance approaches (e.g., Alexander et al., 2000, 2009). In these larger-scale studies, nutrient delivery ratio, *NDR*, along the flow direction is described by first-order kinetics with an effective first-order rate constant, $k_e$ ($T^{-1}$), and a mean hydraulic residence time, $\tau_a$ (T):

$$NDR = \exp[-k_e\, \tau_a] \qquad [2]$$

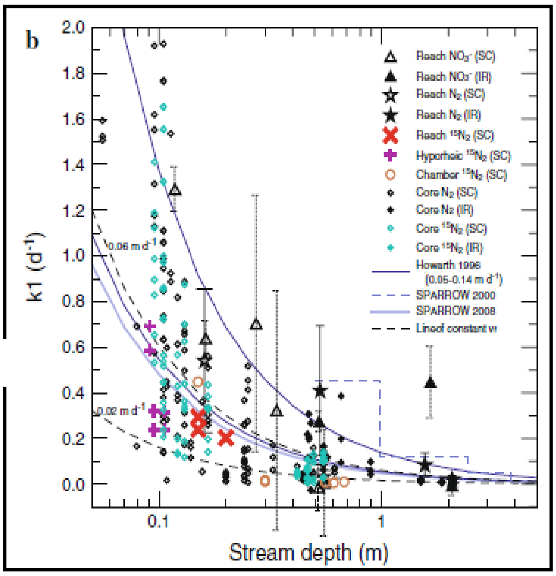


**Figure 5.** Dependence of the effective first-order rate constantfor nitrogen losses, *k1*, on stream depth, *h*. From: Bohlke et al. (2008)

This approach implicitly assumes that the stream reach to act as a single compartment in which nitrate mass is transported through the system by advective flow, and nitrate mass is lost through the combined effects of denitrification and plant uptake. Reported $k_e$ values in these studies vary several orders of magnitude, and there is emerging consensus – based on field observations and numerical modeling analyses – that key hydrological and biogeochemical factors controlling this variability are: river stage ($h$), nitrate concentration ($N$), and temperature ($T$).

Basu et al. (2009) simplified the Transient Storage Model (Bencala and Walters, 1983) by assuming steady state and derived an equation for the effective denitrification rate constant, $k_e$, as a function of hydrologic and biogeochemical controls:

$$k_e[1/T] = \frac{1}{h}\left(\frac{k_{den}}{1/\Delta z + k_{den}/q_B}\right) = \frac{v_f}{h}\left[\frac{L/T}{L}\right] \qquad [3]$$

where $k_{den}$ is a pseudo first-order rate constant ($T^{-1}$); $h$ is the stage (L), which varies with time; $\Delta z$ is the depth (L) of the anoxic sediment zone; $q_B$ is the hyporheic exchange rate ($LT^{-1}$). If denitrification kinetics are nonlinear, $k_{den}$ decreases with increasing nitrate concentration. Also, for transient flow, the hydrologic parameters $h$, $\Delta z$, and $q_B$ vary with time. Note that $v_f$ is the *nutrient uptake velocity* ($LT^{-1}$), as defined by Wollheim et al (2006).

It is evident from Eq (3) that $k_e$ observed in a given system is determined by the biogeochemical factors ($k_{den}$) moderated by two hydrologic factors: the dilution effect ($h/\Delta z$), and the mass-transfer effect ($q_B$). Note that $k_{den}$ is, in turn, controlled by the spatio-temporal variations in DO, DOC, nitrate concentration, and temperature. Eq (3) provides an explanation of the inverse dependence of $k_e$ on stream flow ($Q$) or water depth ($h$), as reported by several investigators (e.g., Alexander et al., 2000; 2009). As an illustration, a data summary compiled recently by Bohlke et al. (2008), is reproduced here (Figure 5); note that *k1* in this graph is $k_e$ according to our notation.

Regression modeling coupled to mass-balance assessments of N export (using the EPA SPARROW model) across the Mississippi River Basin indicate that the effective, first-order denitrification rate constant ($k_e$) decreases with increasing stream depth ($h$) (Alexander et al., 2000) from 0.45 day$^{-1}$ in the headwaters to 0.005 day$^{-1}$. This observation is also supported by data from a few large watersheds around the world (Howarth et al., 1996; Alexander et al., 2000).

Wollheim et al. (2006) suggested that the area-normalized N loss rate – or the uptake velocity, $v_f$ (= $h\ k_e$; units of LT$^{-1}$, or L$^3$L$^{-2}$T$^{-1}$) – as a parameter that is essentially independent of the river size (order), and thus can be used for cross-scale comparisons. The depth-dependence of $k_e$ and the constancy of $v_f$ has been attributed to change in contact area of stream water with benthic sediments along the river network. For $v_f$ to be constant across systems, the combination of terms on the *r.h.s.* of Eq (3) containing $k_{den}$, $\Delta z$, and $q_B$, should be essentially constant (relative to the changes in $h$) for all river orders in a given network. That is, Eq (3) implies that river depth, $h$, functions as the first-order hydrologic control on the observed denitrification rates, while the other parameters in Eq (3) serve as second-order controls in explaining site-to-site variability. For example, a review of denitrification data across systems indicated that $q_B$ varies over a narrow range between 5 to 15 cm/day (Birgand et al., 2006).

## 5. TEMPORAL PATTERNS IN IN-STREAM LOSSES

The analysis referred to in the preceding section is based on "steady state" annual nitrogen mass balances. However, the dependence of nitrate transformation rate constant ($k_e$) on stream stage (*h)* indicates that N losses would also have strong temporal patterns. It is generally acknowledged that over annual time scales, much of the nitrate loss in stream networks occurs during low-flow or base-flow conditions (Alexander et al., 2009), which is consistent with the inverse relationship of $k_e$ with *h*.

Bohlke et al. (2008) examined *hypothetical* within-season variability in stream flow ($Q$, m$^3$s$^{-1}$), temperature (T; $^o$C), and denitrification rate constant (their term: $k1_{denit}$; $T^{-1}$, which is equivalent to our $k_e$) in two streams in dominantly (90-100%) agricultural watersheds (Iroquois River, straddling the border of Illinois and Indiana, USA; and Sugar Creek, in Indiana, USA). They conclude that $k1_{denit}$ (or, $k_e$) values would likely remain at a low during January-June period, increase starting in mid- to late-summer (July-August), peak in mid-fall (September-October), and then decrease in winter (November-December). These patterns are the direct result of seasonal trends primarily in stream flow with the lowest flows and shallow stream depths in fall season, and secondarily in water temperature, with highest temperatures in summer and early fall. These temporal patterns in denitrification rate constant translate to seasonal patterns in nitrate removal efficiency within a stream reach. Alexander et al. (2009) recently modeled these types of patterns in Sugar Creek (Indiana) and Nashua River (Massachusetts). They report that maximum percent nitrate flux reduction within a unit length (km) of a stream reach occurs, as expected, in late summer and early fall.

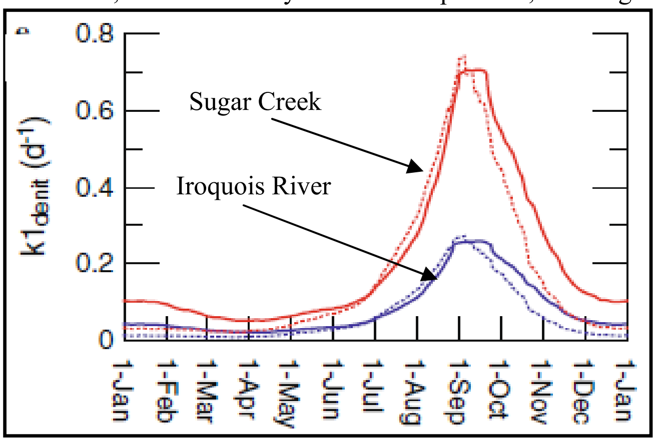


**Figure 6**. Predicted temporal variations in effective rate constant, $k_{1denit}$, for nitrate losses in a stream. (From: Bohlke et al., 2008). Dashed and solid lines indicate predictions with and without temperature correction.

As evident from Eq (2), this temporal pattern in the rate constant is the direct result of two hydrologic factors manifested in the observed biogeochemical process within the sediment: (1) larger $k_e$ due to lower stream depth, *h*; i.e., smaller "dilution effect"; and (2) longer residence time ($\tau_a$) within the stream reach, due to slower stream flows. Note also that in addition to larger flows and higher stages during the spring and early summer seasons, nitrate concentrations (and loads) are larger; thus, further decreases in $k_e$ are expected. That is, nitrate removal efficiency is the lowest when the loads are the largest, which has important implications to downstream impacts, and gives significant clues to how various mitigation approaches may be designed.

## 6. CONCLUSIONS

Intra-annual variability in stream hydrologic conditions (e.g., frequency, duration and magnitude of the stream hydrographs) are directly controlled by the stochastic nature of the climate factors (rainfall patterns, potential evapotranspiration demands), and the landscape (soils, topography, vegetation) attributes. Because of the stochastic nature of the rainfall forcing and the underlying catchment storage-transport processes, the stream flow is intrinsically a random variable. The stochastic variations in flow produce random fluctuations in stream depth ($h$), and thus indirectly induce a random component also in the effective denitrification rate constant ($k_e$). The stream geomorphology controls the relationship between $h$ and $Q$, while the sediment biogeochemistry and the hyporheic zone characteristics control the relationship between $k_e$ and $k_{den}$. We are currently developing the necessary stochastic modeling approaches for theoretical investigation of these types of linkages (Basu et al., 2009b).

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