



## Contaminant Load-Discharge Relationships Across Scales in Engineered Watersheds: Order Out of Complexity

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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<sub>2</sub>O produced during denitrification. The linkage between the hydrologic and the 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 through 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, complicated system rather than natural, complex systems. Thus, in such engineered systems, simpler and more efficient predictive models than currently used are sufficient to describe the hydrologic and biogeochemical responses across scales. Here, we explore three 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<sup>1</sup> to 10<sup>6</sup> km<sup>2</sup>): (1) Can event hydrograph responses within a season be predicted without model calibration? (2) Can nutrient loads within a season be predicted given only information on discharge, use patterns (sources), and attenuation (losses)? (3) Can the in-stream biogeochemical attenuation rates at multiple spatial scales observed for these nutrients be estimated, independent of monitoring data?

We first examined monitoring data available for two large watersheds (700 and 2,000 km<sup>2</sup>) in Indiana, USA, and developed a simple model, TELM (Threshold Exceedance Lagrangian Model), to predict observed event hydrographs and chemographs for four crop growing seasons. TELM predictions, requiring no calibration for model parameters, were in good agreement with the measured event hydrographs and chemographs. TELM model was further tested by comparing predicted event hydrographs and event chemographs measured in the Little Vermillion River watershed (300 km<sup>2</sup>) in Illinois, USA. Next, TELM model outputs were linked to a distributed stream network model, based on Lagrangian travel time distributions, to predict the spatial patterns in nutrient delivery ratios at multiple spatial scales across the watersheds. Furthermore, we examined the hydrologic and water-quality monitoring data available for the Mississippi River Basin, and found consistent linear relationships between area-normalized annual discharge ( $Q; L^3L^{-2}T^{-1}$ ) and area-normalized annual nutrient loads ( $ML^{-2}T^{-1}$ ) at all spatial scales, ranging from first-order watersheds (10 to 100 km<sup>2</sup>) to the entire river basin (3 × 10<sup>6</sup> km<sup>2</sup>), and offer a theoretical explanation. By comparing the load-discharge data for conservative constituents (e.g., bicarbonate) with that for more-reactive constituents (nitrate, phosphate, pesticides), we estimated the effective nutrient attenuation rate constants ( $k_e, T^{-1}$ ) at each spatial scale. Finally, we derived explicit analytical expressions for reproducing the reported  $k_e$  scale-dependence. Implications of these results to watershed management strategies aimed at mitigating adverse water-quality impacts of nutrient loads are discussed.