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Hydrologic context for modelling nutrient cycles

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Interdisciplinary collaboration has become a hallmark of work in the environmental sciences for good reason – the linkages and feedbacks among various components of ecosystems are complex. The sheer heterogeneity of environmental systems is daunting and often leads to understanding that is tailored to a particular field site but lacks generality and transferability. A primary challenge for modern hydrology and environmental sciences is to find ways to learn about patterns at various temporal and spatial scales in the face of heterogeneity and complexity.

One example of such a challenge relates to modeling the nitrogen cycle. The global nitrogen cycle has been perturbed substantially during the anthropocene and gaining an understanding of processes that affect the transport, transformation, and fate of various nitrogen species at a host of time and space scales is critical to inform decisions about how to mitigate effects of nitrogen pollution. In particular, we need to be able to link hydrology with reactive transport of nitrogen and dissolved organic carbon using methods that range from small-scale physics-based models to regression-based models used to "scale up" point processes to regions.

At the plot scale, very detailed models are necessary to capture observed fine-scale dynamics. These models are highly mechanistic and parameter rich. In going to the scale of a hillslope, much of the very detailed biogeochemistry often is subsumed into a much coarser parameterization that can still capture important aspects at that scale. A similar progression occurs as one proceeds to a catchment and then to a regional scale.

Much more work needs to be done to determine better ways to use information developed at small scales to help describe how hydrological and biogeochemical processes interact at catchment and regional scales to produce the effects that are of concern to water managers.

Keywords: *Nitrogen cycle, reactive transport modelling*

1. INTRODUCTION

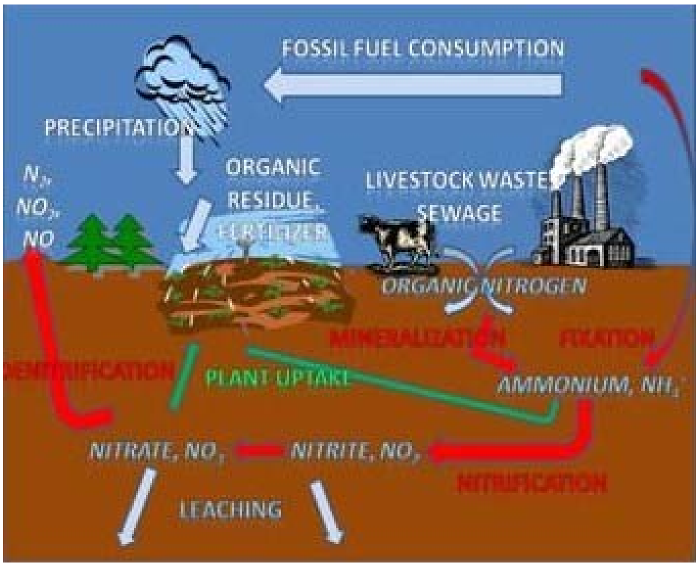

Figure 1. The global nitrogen cycle (simplified).

The global nitrogen cycle is a complex system involving physical transport processes and microbially mediated reactions that convert the various nitrogen species to others (Figure 1). Furthermore, the nitrogen cycle is inextricably linked to carbon and water cycles and so the question of how to describe processes quantitatively is even more vexed than for one cycle alone. Yet such quantitative descriptions are needed to address serious environmental concerns. The natural nitrogen cycle has been perturbed substantially since the Haber–Bosch process led to the widespread use of synthetic fertilizers (Galloway et al., 2003). Among the environmental consequences of the explosion of reactive nitrogen added to the Earth system are atmospheric releases of nitrous oxide, a powerful greenhouse gas, and leaching of nitrate to groundwater and surface water (Vitousek et al., 1997).

The microbially mediated processes such as amonification, nitrification, and denitrification are distributed in soils and sediments in heterogenous patches that result in differing rates of reaction at quite small scales (e.g., McIntyre et al., 2009; Vidon and Hill, 2004). Mathematical models of the processes at the scales of the processes are therefore necessary to gain detailed understanding (Maggi et al. 2008). But the impacts of concern occur at larger scales and so less detailed, lumped models are useful (e.g., Manzoni et al., 2008), models at the watershed scale must be parameterized (e.g., Kimura et al., 2009), and extensions to the global scale must be made (e.g., Adair et al., 2008). In all cases, hydrological processes must be integrated with the biogeochemical nutrient cycling processes *per se*.

2. HYDROLOGICAL IMPACTS ON FATE OF VARIOUS FERTILIZERS

The fate of fertilizers applied to crops and lawns has been studied to reduce both the gaseous losses and the losses by leaching of the fertilizer (e.g., Cameira et al., 2007; Guillard and Kopp, 2004), results that are important for both minimizing fertilizer costs and reducing impacts on air and water quality. Both gaseous and leaching losses depend on irrigation or rainfall rate and timing as well as on the form of fertilizer applied. A reasonably detailed mechanistic model can be used to gain insight into processes that affect the losses. Maggi et al. (2008) describe such a mechanistic nitrogen model, TOUGHREACT-N, that implements nitrogen biogeochemical processes into the fully distributed subsurface water flow and reactive transport model TOUGHREACT (Xu et al., 2005). TOUGHREACT-N simulates the soil N cycle affected by microbial activity,water and fertilizer inputs, and soil type by coupling multiphase advective and diffusive transport, multiple Monod kinetics, and equilibrium and kinetic geochemical reactions.

Gu et al. (2009) extended the model presented by Maggi et al. (2008) by incorporating processes relevant to a variety of ammonia and nitrate forming fertilizers. The model was evaluated in relation to a field experiment in Burgundy, France to simulate 31-day preemergence N losses following multiple types of fertilizer application and subsequently used to examine the effects of application of different fertilizer and soil types and environmental conditions on NO^-_2 and NO^-_3 leaching and on transient NH_3, N_2O, and NO gas emissions.

The set of equations solved by TOUGHREACT-N is rather long and complicated. A very brief summary is presented below; full details can be found in Maggi et al. (2008) and Gu et al. (2009). Flow of water is treated using multiphase flow, taken to be adequately described by the Darcy-Richards equation.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial \psi(\theta)}{\partial z} + 1 \right) \right] \qquad (1)$$

where θ is the soil moisture, and $\psi(\theta)$ and $K(\theta)$ are the water potential and hydraulic conductivity, respectively. Chemical transport is simulated using an advective-diffusive set of equations.

$$\frac{\partial}{\partial t}(\theta_a c_a + \theta_g c_g + \rho_b c_s) = \frac{\partial}{\partial z}\left[\theta_a D_a \frac{\partial c_a}{\partial z} + \theta_g D_g \frac{\partial c_g}{\partial z}\right] - \frac{\partial (v_a c_a)}{\partial z} + S \qquad (2)$$

where c_a, c_g and c_s are the species concentrations in the aqueous, gaseous and solid phases, respectively, θ_a and θ_g are the volumetric fractions of the aqueous and gaseous phase, respectively, ρ_b is the dry bulk density of the solid phase, v_a is the volumetric flux of the aqueous phase, D_a and D_g are the effective diffusion coefficient in the liquid and gaseous phase, respectively, including the effect of tortuosity based on total porosity and phase saturations, S is the source/sink term, t is time, and z is the spatial coordinate. The source-sink term is modeled using multiple Monod kinetics for the nitrogen species and equilibrium speciation calculations for inorganic species. Growth-uptake-conversion equations for three types of microbial populations that perform nitrification, denitrification, and aerobic respiration are included. All in all, more than thirty chemical species are included in the calculations (see Gu et al., 2009). The simulated soil moisture dynamics have a strong influence on predicted soil aerobicity and thus on microbial community dynamics. Hydrological processes largely determine rates at which oxygen can diffuse into the soil and thus the redox state in the profile.

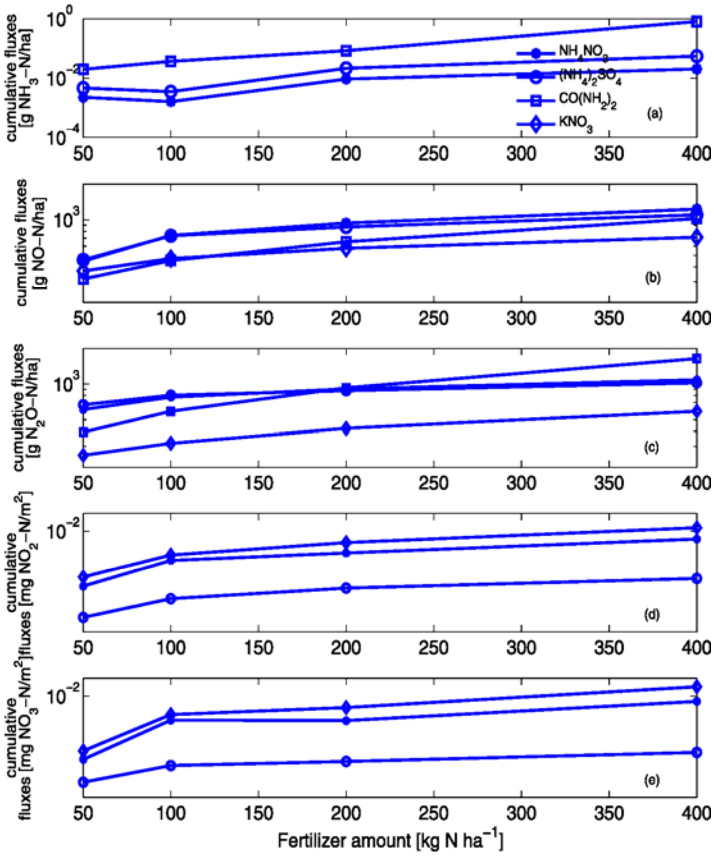

Figure 2. cumulative (a) NH_3, (b) NO, and (c) N_2O surface fluxes to the atmosphere and (d) NO^-_2 and (e) NO^-_3 leachate fluxes at 20 cm for the four fertilizer types as functions of fertilizer amount. The NH_3 volatilization from KNO_3 and the leachate fluxes from $CO(NH_2)_2$ were negligible and thus omitted. From Gu et al., 2009; copyright American Geophys. Union. Reprinted with permission.

Because the model is quite detailed, it can be used to examine the effects of different fertilizer types, different flow regimes, different fertilizer application rates, different soil types, and so forth. For example, consider four different inorganic nitrogen fertilizers applied in solid form – ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2\ SO_4$), urea ($CO(NH_2)_2$), and potassium nitrate (KNO_3). The results show a complex dependence with fertilizer amount, driven primarily by changes in microbial population dynamics under the different regimes (Figure 2). For example, increasing fertilizer amount exaggerates the difference of cumulative solute leaching from fertilizer types. For example, NO^-_3 leaching from KNO_3 is 13 and 1.7 times higher than $(NH_4)_2SO_4$ and NH_4NO_3, respectively, in the 400 kg N ha^{-1} treatment, compared to 7 and 1.2 times in the 100 kg N ha^{-1} treatment (Figure 2, bottom panel).

3. HILLSLOPE-RIPARIAN HYDROLOGICAL EFFECTS

The centimeter-scale simulations that may be appropriate to examine processes at a point in an agricultural field in great detail would be impractical to compute effects observed at larger scales, even the "next larger scale" of a hillslope. An example is a field site on the coastal plain of Virginia, USA where we have done work. At Cobb Mill Creek NO^-_3 concentration in the groundwater is about 10-12 mg N L^{-1} due to leaching of fertilizer from surrounding agricultural fields (Mills et al., 2008). The concentration drops to 1-2 mg N L^{-1} in the stream under base flow as the groundwater traverses the streambed sediments (Mills et al., 2008). The dominant hydrological patterns can be captured with a two-dimensional representation for this case (Figure 3).

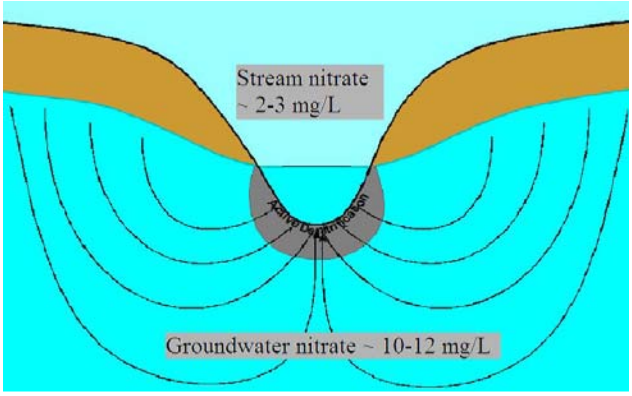

Figure 3. Schematic cross-section of hillslope at Cobb Mill Creek, Virginia, USA.

The hydrological flow for the system can be modeled using equations for variably saturated flow (Gu et al. 2008).

$$\frac{\partial}{\partial x_i}\left(K_r K_i \frac{\partial h}{\partial x_i}\right) = \left[S_w S_s + C(\psi)\right]\frac{\partial h}{\partial t} \qquad (3)$$

where x_i represents the horizontal and vertical coordinate directions, K_i represents the principal components of the hydraulic conductivity tensor, aligned to be collinear with the horizontal and vertical directions, K_r is relative permeability, assumed to be a scalar function of water saturation, S_w is water saturation, which varies between 0 for dry conditions and 1 for saturated conditions, S_s is specific storage, h is hydraulic head, C is specific moisture capacity, ψ is pressure head, equal to h–z, where z is elevation head, and t is time [T]. For this application, we consider equations for only aqueous species.

$$\frac{\partial c_k}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ii}\frac{\partial c_k}{\partial x_i} + \theta D_{ij}\frac{\partial c_k}{\partial x_j}\right) - q_i \frac{\partial c}{\partial x_i} - S \qquad (4)$$

where c_k is concentration of solute k, D_{ij} is the hydrodynamic dispersion tensor, q is specific discharge, θ is effective porosity, and S is the source-sink term that accounts for biogeochemical reactions. Full details of the model can be found in Gu et al. (2008) and Gu et al. (2007).

A finite-element model is used to solve the equations with a finer grid near the stream where the reactions are concentrated (Figure 4). On the basis of the total groundwater discharge and NO^-_3 reduction, we calculate a removal rate of nitrate-nitrogen in the biogeochemically reactive zone around the channel of more than 3 g $m^2 d^{-1}$ (Gu et al., 2008). With a sufficient carbon source, the sediments near the groundwater-surface water interface possess a remarkable potential for nitrate removal from subsurface waters.

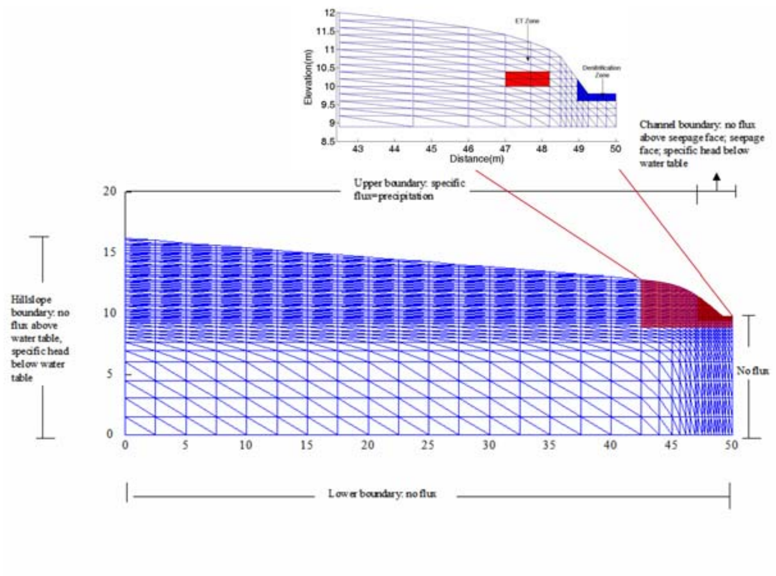

Figure 4. Finite element meshes for the Cobb Mill Creek transect. The flow model used the entire domain; the transport model used the shaded subdomain. From Gu et al., 2008; copyright American Geophys. Union. Reprinted with permission.

The model is easily extended to study transient effects caused by passage of a flood wave. The changing stream stage leads to an interaction between the stream and the groundwater that changes residence time in the sediments where the kinetically controlled denitrification reactions take place. The longer residence times at peak flow relative to base flow indicate that the reactions proceed farther in the former case, i.e., that more nitrate is removed during a freshet than during base flow (Gu et al., 2008).

4. THE CATCHMENT SCALE

Computation at the catchment scale often is accomplished with lumped models. Under a set of assumptions that are reasonable for forested upland catchments, flow can be considered to be driven strongly by topography. In such catchments infiltration rates typically are high enough that all precipitation infiltrates and overland flow occurs only in saturated areas near the stream. Under such conditions TOPMODEL (Beven and Kirkby 1979) provides a reasonable framework for catchment modeling.

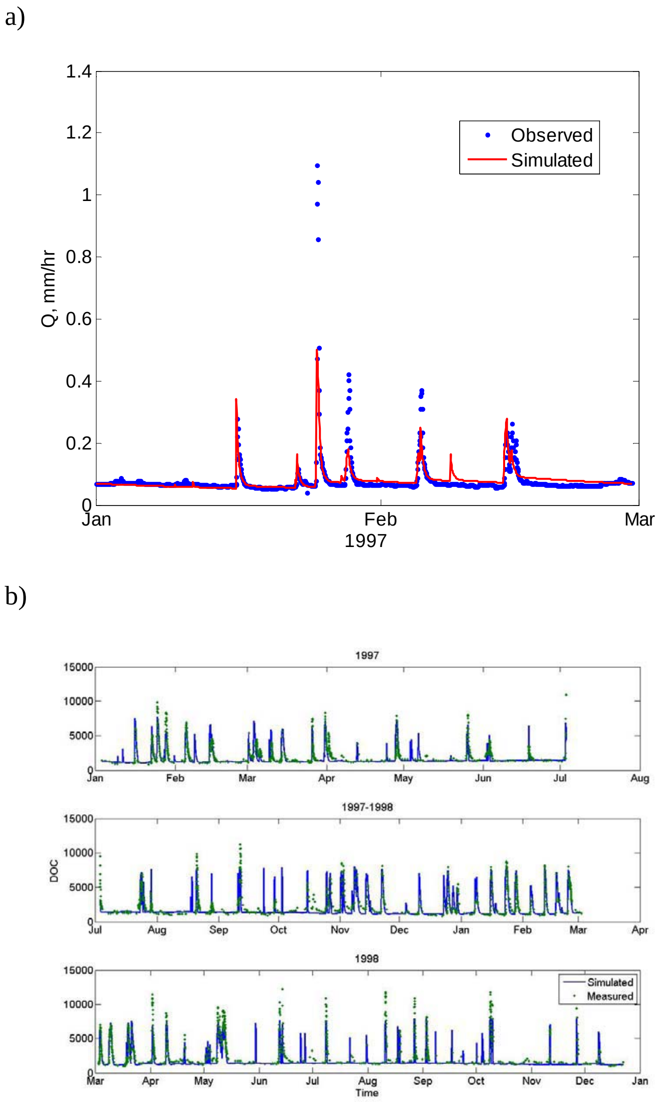

Figure 5. a) Segment of WCC hydrograph simulated with TOPMODEL and b) DOC simulated using TOPMODEL flow components.

We applied TOPMODEL to simulate the recorded hydrograph for White Clay Creek (WCC) near Avondale, Pennsylvania, USA. The Stroud Water Center is located on WCC and biogeochemical processes have been studied in the catchment for many years (Newbold et al., 1997). The basic idea is to use the hydrological model to decompose the total flow into components and then “mix” the nutrients appropriately to mimic the observed chemical dynamics. The analysis of streamflow recession curves for WCC suggests that more than one “reservoir” is contributing to streamflow. The original TOPMODEL has saturation excess overland flow and a single subsurface stormflow reservoir. Therefore, it was decided to use a modified version of TOPMODEL that has a groundwater component as well as a subsurface stormflow reservoir (Scanlon et al., 2000). The hydrograph can be simulated with reasonable success (Figure 5a) and a simple mixing model using the simulated flow components represents the dynamics of dissolved organic carbon (DOC) fairly well (Figure 5b).

For WCC, the storm dynamics are such that a model that mixes DOC conservatively is adequate so there is no issue of scaling biogeochemical reaction kinetics to the catchment scale. At a seasonal or annual time scale, kinetics are important of course, and must be incorporated into the model. For example, in modeling the snowmelt-dominated Snake River in Colorado, USA, we accounted for buildup of DOC in the soil due to microbial activity, using a simple temperature modulated first-order rate law as the simplest approximation of the more complicated source-sink term in the hillslope nitrogen model sketched above, which itself was a simplification of the more complex dynamics described in the TOUGHREACT-N model applied to the plot scale (Hornberger et al., 1994).

5. EXTENSION TO REGIONS

Researchers at the U.S. Geological Survey have extensively developed a SPAtially Referenced Regressions on Watershed Attributes (SPARROW) model to calculate nutrient loads on a regional basis (Smith et al., 1997). SPARROW is a nonlinear regression model and accounts for nutrient loss due to land-surface and instream processes as well as land use and land surface characteristics. The model includes parameters for instream processes that remove nitrogen and wetland area can be included as a regression variable. In this way, some account may be taken of the extensive denitrification that occurs at locations such as Cobb Mill Creek. The application is necessarily coarse grained, however. For example, the model as applied to the Eastern Shore of Virginia, USA, where Cobb Mill Creek is located, indicates uniformly high nitrogen loading for streams (Preston and Brakebill, 1999) contrary to observations (Mills et al. 2008).

6. DISCUSSION

The environment is extraordinarily heterogeneous at essentially all scales of interest. The processes at Cobb Mill Creek at the hillslope scale that we describe using a set of kinetic biogeochemical parameters derived from laboratory experiments, for example, aggregate a host of spatial and temporal variations. We installed dense grids of seepage meters in several reaches of Cobb Mill Creek to investigate spatial patterns of nitrate removal across the channel cross section. We measured the rates of groundwater seepage and the concentrations of nitrate and chloride in groundwater discharging from the streambed at the site to examine the spatial heterogeneity (Flewelling et al. 2007). The data indicate that certain areas of the streambed are dominated by vertical upwelling of deep groundwater where denitrification is the primary cause for nitrate removal. Other portions of the streambed receive groundwater that flows through the riparian zone where plant uptake and evapo-concentration may also be important in nitrate dynamics. Thus, even the relatively mechanistic model we use for the hillslope processes is, in effect, a lumped model because the kinetic coefficients represent some average over a quite heterogeneous landscape. Furthermore, a synoptic survey of 16 streams in the vicinity of Cobb Mill Creek reveals nitrate concentrations ranging from about 1 to 7 mg/L under baseflow conditions with no apparent strong relationship to land cover, land use, or other characteristics that might explain the variability (Mills, AL, University of Virginia, unpublished data; Mills et al. 2002). Much more work needs to be done to determine better ways to use information developed at small scales to help describe how hydrological and biogeochemical processes interact at catchment and regional scales to produce the effects that are of concern to water managers.

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