INVITED COMMENTARY

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Nutrient limitation, hydrology and watershed nitrogen loss

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Introduction

Forty years ago scientists framed the small-watershed concept to examine how ecological and hydrological processes interact to regulate biogeochemical cycling in terrestrial ecosystems (Likens and Bormann, 1995). This approach inspired new ways of thinking, particularly at the watershed scale, about what controls nutrient losses from terrestrial ecosystems. How can we continue to link ecology and hydrology to provide new insights into long-standing, fundamental questions in biogeochemistry? At least one approach would be to frame questions that are consistent with an understanding of nutrient limitation—its causes and consequences—in terrestrial ecosystems.

Nutrient limitation as a scientific concept originated in 19th century agricultural chemistry, and it continues to serve as an organizing principle in modern biogeochemistry. A limiting nutrient is defined as that element in shortest supply relative to demands for plant growth. The addition of a limiting nutrient will stimulate plant growth (i.e. net primary productivity) more than will additions of any other elements, and co-limitation by two or more nutrients is also possible.

Nitrogen (N) is the most common limiting nutrient in the temperate zone, as indicated by its widespread use in agricultural fertilizers, and by experimental additions of nutrients to a range of natural terrestrial ecosystems (Vitousek and Howarth, 1991). Limitation by N is common in so many regions because it is not supplied by rock weathering (with few exceptions), and must accumulate from atmospheric deposition and biological fixation as ecosystems develop. With sustained inputs of N from atmospheric deposition (especially air pollution) and biological fixation, it is possible to overcome limitation by N, though experimental tests of limitation by nutrients other than N are rare for temperate terrestrial ecosystems (see Tanner *et al.* (1998) for a brief review of tropical forests).

Nitrogen limitation has important consequences for the cycling and loss of N from watershed ecosystems. Plants and their mycorrhizal associates rapidly assimilate plant-available forms of N (i.e. NH_4^+, NO_3^-, simple amino acids) in N-limited ecosystems, and retain this N by conversion to more complex organic forms. Microbial communities in soils release available N during organic matter decomposition; however, they can assimilate it almost as rapidly in order to satisfy metabolic requirements for the decomposition of low-N litter. In this way, nutrient limitation drives tight retention of

plant-available N, and leads to only very low losses of plant-available N for most of the time from N-poor temperate watersheds (Perakis and Hedin, 2001, 2002).

A longer-term view, however, finds the ecosystem N cycle considerably more open than is often appreciated (e.g. Peterjohn and Schlesinger, 1990; Vitousek and Field, 2001). For example, consider that natural N inputs to temperate forests from asymbiotic N fixation and atmospheric deposition are $\sim$4 kg ha^{-1} year^{-1} (Cleveland *et al.*, 1999; Holland *et al.*, 1999). Over 12 000 years of post-glacial development, this provides an opportunity for 48 000 kg ha^{-1} of N to accumulate in soils and vegetation (substantially more could accumulate in unglaciated regions, or with symbiotic fixation included). However, most studies report ecosystem N accumulations of only $\sim$5,000 kg ha^{-1}. Where did the other 43 000 kg ha^{-1} of N (90% of inputs) go? Better estimates of N in deep soils and riparian areas would account for some missing N. Fires, landslides, harvest, and other severe disturbances can drive N loss in some regions, yet these pathways are not universal to all ecosystems at all times. Other, more general, pathways of N loss must be important, and losses related to hydrology would seem a good candidate. But how can such N losses occur from N-limited ecosystems? Here is where some new thinking about interactions between hydrologic and biogeochemical cycles opens up possibilities for, and sets limits to, losses of N from N-limited watersheds.

Open hydrologic and biogeochemical cycles

'Open cycle' invokes a paradox, yet hydrologic and biogeochemical cycles are certainly open at the level of ecosystems. Both water and nutrients cross ecosystem boundaries, and their cycles are more open when throughput is large relative to storage. Hydrologic cycles can be especially open in small watersheds, where a large fraction of precipitation inputs is lost quite rapidly. Plant-associated biotic processes can close the hydrologic cycle through water uptake and storage that delays runoff (particularly in arid areas), yet they can also accelerate it by promoting inputs from fog and losses via transpiration. Biotic processes generally close cycles of essential elements more than they close hydrologic cycling, and do so in proportion to the degree of nutrient limitation (Vitousek and Reiners, 1975). Where ecosystems approach long-term steady-state levels of biomass and organic matter accumulation, biogeochemical cycles may continue to close by narrowing of stoichiometric ratios in organic matter, and by formation of insoluble precipitates in soils.

The relative openness of hydrologic *versus* biogeochemical cycles promotes nutrient loss from watersheds. Water is the main vector of solute and solid movement for most mineral elements under most conditions, and in the absence of catastrophic disturbances, water flux sets the upper limit for openness of many element cycles (e.g. Cl); that is, solutes can be lost only as fast as water will allow. Biogeochemical mechanisms of nutrient retention can slow element losses, and consequently the cycles of growth-limiting nutrients (e.g. N and P) may appear especially closed relative to that of water. On the other hand, elements with a significant gaseous phase may cycle and be lost independent of, or even faster than, the limit set by hydrology—though biotic uptake typically restricts gas-phase losses of biologically important nutrients from upland systems (e.g. of N, S). Thus, at the level of entire watershed-ecosystems, the openness of essential element cycles is bounded on one side by the hydrologic cycle and on the other by biological and geochemical retention.

Hydrologic control of watershed nitrogen loss

Despite the complexity of N cycling processes within an ecosystem, it is reasonable to consider that N limitation imposes one overarching and relatively simple constraint on potential losses of N from watersheds: N losses must occur via pathways that N-limited plants are unable to control. Current research identifies three pathways of 'uncontrollable' N loss that may occur from N-limited ecosystems: (1) losses of N as dissolved organic N (DON) forms that are unavailable for immediate plant uptake; (2) losses of plant-available N that occur due to temporal or spatial imbalances between N supply and demand;

and (3) losses of trace N gases produced during nitrification in soils. These uncontrollable pathways of N loss are of great interest to ecologists, since, over long time scales, they may contribute to the development and maintenance of N limitation in a wide range of temperate terrestrial ecosystems (Hedin *et al.*, 1995; Vitousek *et al.*, 1998, Vitousek and Field, 2001; Perakis and Hedin, 2002). Hydrologic processes matter quite a bit for each of these pathways of N loss, and provide exciting opportunities for hydrologic and ecological collaborations to address fundamental questions at the core of biogeochemical theory.

DON represents perhaps the largest uncontrollable N flux from temperate watersheds. The relative openness of the hydrologic cycle promotes loss of DON before its decomposition and retention as plant-available N within ecosystems (Hedin *et al.*, 1995). At the global scale, there is a need to understand how hydrologic components of the climate system influence long-term interactions between soil organic N accumulation, DON loss, and N limitation (Schimel *et al.*, 1997). DON losses from watershed ecosystems can vary substantially across the landscape—much more so than nitrate in unpolluted regions (Perakis and Hedin, 2002)—and there is a fundamental need to understand the causes and consequences of such variation for how watershed ecosystems work.

There is good evidence that fluxes of DON *within* ecosystems depend on rates and timing of hydrologic cycling well (Michalzik *et al.*, 2001). Watershed losses of DON are harder to predict, however, in large part due to inadequate information on what controls DON cycling along soil hydrologic flowpaths. As with dissolved organic carbon, percolation through mineral soils promotes net removal of DON via sorption and biotic uptake, and thus closes solute cycling relative to that of water. Detailed knowledge of how DON retention varies as a function of flowpath, water residence time, mineralogy, DON composition, and other factors is sorely needed. Hydrologic conditions that decrease the residence time of water in mineral soils, or which promote clay formation and decreased percolation through mineral soils, may short circuit DON directly from surface soils

(Frank *et al.*, 2000), and thus intensify N loss and limitation across gradients from dry to wet ecosystems (Perakis and Hedin, 2002).

Open hydrologic cycles can also promote the loss of plant-available forms of N from N-limited ecosystems. In most ecosystems for most of the time, plant demands for N are synchronized to N release from decomposing organic matter, resulting in only low losses of available N. However, variations in the hydrologic cycle can promote asynchrony in N cycling via physiological, phenological, or other temporary resource limitations (e.g. light) on plant N uptake. Such asynchrony can occur over episodic, seasonal, and annual time scales to foster temporary accumulation of excess plant-available N in soils, and its loss from ecosystems that are otherwise N limited (Vitousek and Field, 2001). Episodic losses of available N occur at least some of the time in a wide range of temperate terrestrial ecosystems (e.g. deserts, grasslands, woodlands, forests), and current watershed biogeochemistry process models describe asynchronous N losses better than other uncontrollable N loss pathways (e.g. Creed *et al.*, 1996; Aber and Driscoll, 1997; Band *et al.*, 2001). However, the occurrence of plant available N losses during the growing season of many N-limited ecosystems may also betray a bias of incipient N saturation (see below).

Nitrification transformations internal to the soil N cycle can also drive uncontrollable losses of N via production of trace N gases, i.e. NO and N_2O (Davidson and Firestone, 1989). Both autotrophic (i.e. oxidation of NH_4^+ to NO_3^-) and heterotrophic (i.e. conversion of simple organic N to NO_3^-) nitrification are important processes that promote gaseous N loss, though the former often dominates in N-rich ecosystems and is reduced by plant competition for available N (Zak *et al.*, 1990). Hydrology can influence nitrification via indirect effects on soil moisture, which regulates the diffusion of nitrification substrates and the activity of nitrifying soil microbes (Stark and Firestone, 1995). Since trace N gases are important contributors to radiatively active 'greenhouse' gases (Matson, 1997), their emission may also impact hydrologic cycles through feedbacks in the Earth climate system.

Human–dominated ecosystems and theories

Humans have accelerated N cycling in many ways and in many places on Earth (Vitousek *et al.*, 1997). This acceleration influences both the nature of ecosystem N loss and our perception of what controls these losses. For example, studies from disturbed and/or polluted regions report wide variations in nitrate loss as a function of plant community composition, diversity, climate, topography, soil type, and other important ecosystem attributes (Tilman *et al.*, 1996; Creed and Band, 1998; Goodale *et al.*, 2000, Lovett *et al.*, 2000). In contrast, temperate watersheds that are historically free from significant human impact show only negligible variation in nitrate loss despite wide differences in ecosystem attributes (Perakis and Hedin, 2002). This disparity raises the possibility that human activities may have altered watershed N losses from temperate ecosystems in ways that are more subtle, and more pervasive, than previously recognized. There is great appeal in identifying 'baseline' ecosystems and the controls therein that shape natural variability in watershed N losses. Increasingly, we need to consider how widespread and historical human impacts may introduce unintended bias into what we perceive as baseline ecosystems, and into how we construct and test theories using these baselines (Hedin *et al.*, 1995).

The hydrologically driven pathways of uncontrollable N loss described above are susceptible to such bias, particularly for ecosystems in transition from N-limited to N-saturated status. As an example, losses of plant-available N are low for most of the time from N-limited ecosystems, yet modest increases in N input may amplify supply/demand imbalances that accentuate synchronous nitrate losses by hydrologic flushing. Continued and chronic N inputs may, however, result in consistently elevated losses of nitrate, with little or no sensitivity to hydrologic flushing (Stoddard, 1994). These complex interactions between hydrology and N cycling are fascinating, and have attracted substantial scientific attention—yet in most cases we have ignored the analogous response of DON—even when DON quantitatively dominates over nitrate as a vector of watershed N loss.

A more durable view for the future will need to reconcile theories that emphasize nitrate loss variation with the possibility that much of this variation could be an artifact of human-dominated N cycling.

Closing thoughts on open cycles

Widespread N limitation promotes strong biotic demands for N, which has direct consequences for preventing hydrologic losses of N from most ecosystems for most of the time. In turn, hydrology strongly influences N cycling in ways that promote the loss of N via pathways that are not under direct biological control, and which contributes to widespread N limitation. This two-way street of interactions between N loss and N limitation provides fascinating opportunities for future collaborative research between hydrologists and ecologists. Appreciation of how these interactions occur in time can guide these efforts: biota reflect the degree of N limitation rather immediately, and restrict forms and timing of N loss in an almost instantaneous fashion when conditions are favourable for growth. In contrast, hydrologically driven N loss may take centuries to millennia to influence N limitation in any substantive way, since annual losses are small compared with soil N reserves. Observations, models, and experiments can all contribute to unravelling these interactions, both from fundamental perceptions and theories of how hydrology and ecology interact to control biogeochemistry, and also in light of substantial real-world changes in watershed N cycles that result from human activities.

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