Factoring stream turbulence into global assessments of nitrogen pollution

Title: Factoring Stream Turbulence into Global Assessments of Nitrogen Pollution

One Sentence Summary: A previously overlooked upper limit on nitrate uptake in headwater streams informs stream restoration and local-to-global nitrogen budgets.

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Abstract: The discharge of excess nitrogen to streams and rivers poses an existential threat to both humans and ecosystems. A seminal study of headwater streams across the U.S. concluded that in-stream removal of nitrate is controlled primarily by stream chemistry and biology. A reanalysis of these data reveals that stream turbulence (in particular, turbulent mass transfer across the concentration boundary layer) imposes an upper limit on the rate nitrate is removed

from streams. The upper limit correctly predicts nitrate removal in streams with low levels of nitrate pollution, a discovery that should inform stream restoration designs and efforts to assess the impacts of nitrogen pollution on receiving water quality and the global nitrogen cycle.

Main Text: Over the past century humans have dramatically increased nitrogen loading to streams and rivers, primarily from the over-application of fertilizer for food production. The environmental consequences of this nitrogen pollution are evident in both developed and developing countries, and include eutrophication of inland and coastal waters, ocean acidification, and greenhouse gas generation (*1,2*). Thousands of stream, river, lake, groundwater, and coastal sites across the U.S. are classified as impaired for nitrogen by the U.S. Environmental Protection Agency (*3*). In a recent assessment of critical earth systems required for the continued development of human societies, nitrogen pollution was identified as one of only three planetary boundaries (along with phosphorous pollution and loss of genetic diversity) that have already been crossed (*4*). According to the U.S. National Academy of Engineering, restoring balance to the nitrogen cycle is one of the 14 Grand Challenges facing engineers in the 21st Century (*5*).

Streams have a natural capacity to remove dissolved inorganic nitrogen (DIN, including nitrate, nitrite, and ammonium) through a coupling of physical transport processes and biologically mediated reactions in streambed sediments (**Fig. 1A**). DIN is assimilated by autotrophs growing at the sediment-water interface (benthic algal layer) and heterotrophic microbial populations in the hyporheic zone (*6*), a region of the sediment bed where hydrologic flow paths begin and end in the stream (*7*). As DIN travels through the hyporheic zone it undergoes a variety of microbially mediated redox reactions including oxidation of ammonium to nitrate (nitrification) and reduction of nitrate to nitrite, nitrous oxide, and di-nitrogen

(denitrification). Of these, only denitrification permanently removes nitrogen from the stream through the evasion of nitrous oxide or di-nitrogen gas. Indeed, the production of nitrous oxide by streams is approximately 10% of global anthropogenic emissions of this potent greenhouse gas (*8*), of which headwater streams account for a disproportionate fraction (*2*). Of the DIN that is assimilated, a fraction is stored (for >1 year) as particulate nitrogen in streambed sediments or in adjacent riparian vegetation (*9*) while the rest is re-mineralized and released back to the stream.

The local efficiency with which DIN is removed from a stream can be quantified by one of several nutrient spiraling metrics (*10*). In this study we focus on nitrate (because of its mobility, recalcitrance, and environmental impacts) and quantify its removal with the nitrate uptake velocity $v_f \geq 0$ (units m s^{-1}), defined as the flux of nitrate into the streambed divided by the concentration of nitrate in the overlying water column.

The second Lotic Intersite Nitrogen eXperiment (LINX II), which was conducted over five years from 2001 to 2006, remains one of the most comprehensive studies of nitrate uptake in headwater streams to-date (*6*,*8*,*11*,*12*). LINX II included ^{15}N-labeled nitrate seeding experiments in 72 streams across eight regions of the U.S., collectively representing eight different biomes (temperate rain forest, chaparral, northern mixed forest, deciduous forest, montane coniferous forest, temperate grassland, shrub desert and tropical forest) and three different land-use types (reference streams, urban streams, and agriculture streams). Based on regression and structural equation modeling of these data, LINX II researchers concluded that the nitrate uptake velocity is controlled primarily by stream chemistry (ambient concentrations of nitrate and ammonium) and biology (gross primary production and ecosystem respiration), and only weakly by stream physics (residence time in the hyporheic zone). Similarly, a meta-analysis of nutrient spiraling

experiments conducted over the past three decades concluded that the evidence for physical controls on nutrient uptake in streambed sediments is "equivocal" (*10*).

Evaluation of physical controls on nitrate uptake in streams have focused on hyporheic exchange (circulation of water through the hyporheic zone), quantified based on transient storage analysis of conservative tracer injection experiments (*13*) or physical models of the pumping of water through streambed sediments by static and dynamic pressure variations (*7*). Missing from these previous assessments is turbulent mass transport across the concentration boundary layer at the bottom of a stream. This transport mechanism is a key control on the delivery of oxygen to fine-grained (non-permeable) sediments (*14*), although its importance in streams with coarser (permeable) sediments (like most of the headwater streams included in the LINX II study) is not clear (*15*).

Given its position between the stream and streambed (**Fig. 1A**), we hypothesized that nitrate uptake by permeable sediment beds might be "bottlenecked" by turbulent transport across the concentration boundary layer. In that event, the uptake velocity can be expressed as the product of a mass transfer coefficient k_{m} that depends solely on stream physics (the velocity with which mass is "squeezed" across the concentration boundary layer by turbulence, units m s^{-1}) and an efficiency α that captures the coupled hydrogeology and biogeochemistry of nitrate uptake in the benthic algal layer and hyporheic zone (the fraction of nitrate delivered to the streambed removed by assimilation and denitrification, unitless) (derivation in Supplemental Materials):

$$v_{\mathrm{f}} = \alpha k_{\mathrm{m}},\ v_{\mathrm{f}} \geq 0,\ 0 \leq \alpha \leq 1,\ k_{\mathrm{m}} \geq 0 \tag{1a}$$

$$\alpha = 1 - \frac{1}{\mathrm{Da}_{\mathrm{bl}} + 1},\ 0 \leq \mathrm{Da}_{\mathrm{bl}} < \infty \tag{1b}$$

$$\mathrm{Da}_{\mathrm{bl}} = \frac{v_{\mathrm{bed}}}{k_{\mathrm{m}}} = \frac{\text{nitrate uptake velocity in the streambed}}{\text{turbulent mass transport across concentration boundary layer}} \qquad (1c)$$

Conceptually, the mass transfer coefficient k_{m} represents the potential (mass-transfer limited) uptake velocity of a stream while the efficiency α indicates the fraction of that potential realized in practice. The efficiency depends on a dimensionless Damköhler number $\mathrm{Da}_{\mathrm{bl}}$ representing the balance of nitrate uptake in the streambed (v_{bed}, units m s^{-1}) by assimilation and denitrification and mass transfer across the concentration boundary layer by stream turbulence; the subscript on $\mathrm{Da}_{\mathrm{bl}}$ indicates that it applies to the concentration boundary layer. Because efficiency α varies from 0 ($\mathrm{Da}_{\mathrm{bl}} \to 0$) to 1 ($\mathrm{Da}_{\mathrm{bl}} \to \infty$), if our hypothesis is correct the uptake velocity should always be less than or equal to the mass transfer coefficient: $v_{\mathrm{f}} \le k_{\mathrm{m}}$ (see equation (1a)).

As a test of our hypothesis, we estimated values of the mass transfer coefficient at all LINX II sites where uptake velocities by both assimilation and denitrification ("total uptake", $v_{\mathrm{f,tot}}$, units m s^{-1}) and denitrification alone ("denitrification uptake", $v_{\mathrm{f,den}}$, units m s^{-1}) were reported (69 and 49 of the 72 LINX II sites, respectively) (*6,11,12*). Site-specific values of the transfer coefficient k_{m} were estimated from surface renewal theory, assuming mass transport across the concentration boundary layer occurs by sweep and ejection events associated with coherent turbulence in the stream together with molecular diffusion of mass into the streambed (*16*). This theory predicts that k_{m} can be calculated from routinely measured features of a stream including slope (S) and depth (h), together with temperature-corrected values for the kinematic viscosity of water (υ, units m^2 s^{-1}) and the molecular diffusion coefficient of nitrate in water (D_{m}, units m^2 s^{-1}):

$$k_{\mathrm{m}} = 0.17 u_{*} \mathrm{Sc}^{-2/3} \tag{2a}$$

$$\mathrm{Sc} = \upsilon / D_{\mathrm{m}} \tag{2b}$$

$$u_{*} = \sqrt{g h S} \tag{2c}$$

The Schmidt number (Sc, unitless) represents the relative importance of molecular diffusion of momentum and mass, the shear velocity (u_{*}, units m s^{-1}) is a measure of stream turbulence, and gravitational acceleration is $g = 9.81$ m s^{-2}. Very similar formulae for calculating the mass transfer coefficient (equation (2a)) are obtained for different conceptual models of the sediment-water interface (e.g., rough versus smooth) (reviewed in (*15*)).

With few exceptions, the LINX II total and denitrification uptake velocities conform to the inequality $v_{\mathrm{f}} \leq k_{\mathrm{m}}$ predicted by surface renewal theory (**Figs. 1B** and **1C**). The implied removal efficiencies (computed from the ratio $\alpha = v_{\mathrm{f}} / k_{\mathrm{m}}$) span approximately three ($10^{-4} < \alpha_{\mathrm{den}} < 0.1$) and four ($10^{-4} < \alpha_{\mathrm{tot}} \leq 1$) orders of magnitude for denitrification and total uptake, respectively (**Fig. 1D**). The reduced range for α_{den} probably reflects the more restrictive nature of denitrification, which requires the presence of microbial populations capable of catalyzing the relevant redox reactions, anoxic conditions in the sediment, and sufficient electron donor and nitrate concentrations (*9,11,12*). For the few exceptional sites that do not conform to the inequality $v_{\mathrm{f}} \leq k_{\mathrm{m}}$, the total uptake velocity exceeds the mass transfer coefficient by factor of two or less; well within the uncertainty of the methods used to estimate the mass transfer coefficients (*15*) and uptake velocities (*11*).

Removal efficiencies calculated from the LINX II data do not exhibit a consistent relationship to catchment land-use (**Fig. 1D**), but they are negatively correlated with stream

nitrate concentration (**Figs. 2A and 2B**). In one of the most influential findings to come out of the LINX II study, a similar negative correlation was observed between nitrate uptake velocity and stream nitrate concentration (*11*). As noted by Mullholland et al., the negative correlation implies that an increase in nitrate load to a stream could elicit "a disproportionate increase in the fraction of nitrate that is exported to receiving waters" (*11*). Our hypothesis provides a mechanistic explanation for this key the LINX II finding: uptake velocities are highest in streams with low nitrate concentration because, under such conditions, all nitrate that comes into contact with the streambed is removed by assimilation and denitrification ($\alpha_{\mathrm{tot}} \approx 1$ when $\left[\mathrm{NO}_3^-\right] < 10^{-3}$ mol m^{-3}, see **Fig. 2A**) and as a result the nitrate uptake velocity is mass-transfer limited ($v_{\mathrm{f,tot}} \approx k_{\mathrm{m}}$). With increasing nitrate concentration, a smaller fraction of the nitrate delivered to the streambed by turbulence is removed (α_{tot} declines with increasing $\left[\mathrm{NO}_3^-\right]$), presumably because sediment-associated autotrophic and heterotrophic organisms are progressively nitrate saturated. Denitrification efficiencies α_{den} calculated from the LINX II dataset follow a similar trend (compare panels **A** and **B**, **Fig. 2**); indeed, across all stream sites sampled in the LINX II study, the denitrification efficiency is a roughly constant fraction of the total efficiency ($\alpha_{\mathrm{den}} \approx 0.14\alpha_{\mathrm{tot}}$) (*17*).

Our hypothesis also implies a simple scaling relationship for the fraction of nitrate removed ($0 \le f \le 1$) over a stream reach of length L (units m) (*18*).

$$f = 1 - \exp\left(-0.17\alpha\sqrt{\frac{f_{\mathrm{D}}}{8}}\left(\frac{L}{h}\right)\mathrm{Sc}^{-2/3}\right) \qquad (3)$$

If the goal is to enhance potential nitrate removal by manipulating stream physics (e.g., through stream restoration) equation (3) indicates that the Darcy-Weisbach friction factor

$f_D = 8u_*^2/U^2$ (where U (units m s^{-1}) is the average velocity of the stream) and the length-to-depth ratio L/h should be maximized; e.g., using conventional hydraulic relationships (*19*). When stream nitrate concentrations are low (i.e., $\left[NO_3^-\right] < 10^{-3}$ mol m^{-3}) nitrate removal is mass-transfer limited and therefore the removal efficiencies can be approximated by the following fixed constants: $\alpha_{tot} \approx 1$ and $\alpha_{den} \approx 0.14$ (**Fig. 2**). For stream nitrate concentrations above this threshold, the results in **Fig. 2** imply that nitrate removal is rate-limited by N-cycling and transport within the sediment bed, not by stream turbulence. Under such conditions several options are available for estimating α_{tot} and α_{den}. The simplest involves substituting into equation (3) the linear correlations between log-transformed efficiency and log-transformed nitrate (see lines in **Fig. 2**). When applied to the LINX II dataset, this approach closely reproduces empirical distributions of nitrate removal by assimilation and denitrification (f_{tot}) but overestimates nitrate removal by denitrification alone (f_{den}) (**Fig. 3A**). This approach also performs poorly when evaluated on a site-by-site basis (**Fig. 3B**, Nash-Sutcliff Efficiency -0.3 and $E = 0.0$ for f_{tot} and f_{den}, respectively, where $E = 1$ is a perfect model fit and $E < 0$ is worse than the mean), implying that there is plenty of room for model improvement. One promising approach along these lines involves coupling the turbulent mass transfer theory presented here with process-based models of N-cycling and transport in the benthic algal layer and hyporheic zone (*20*,*21*); two examples are provided in Supplemental Materials. By incorporating equation (3) into stream network models, like the one recently prepared for the Mississippi River Basin (*22,23*), predictions of in-stream nitrate removal can be scaled-up to reach, catchment, continental, and global scales.

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17. The linear regressions presented in Fig. 2 (see legend) can be expressed as follows: $\alpha_{\mathrm{den}} = 10^{-3.36}\left[\mathrm{NO}_3^-\right]^{-0.49}$ and $\alpha_{\mathrm{tot}} = 10^{-2.5}\left[\mathrm{NO}_3^-\right]^{-0.49}$. The claim that $\alpha_{\mathrm{den}}/\alpha_{\mathrm{tot}} \approx 0.14$ follows directly from taking the ratio of these two power-laws.

18. We derived equation (3) by performing mass balance over a stream reach assuming steady uniform flow: $f = 1 - \exp(-v_f / H_L)$ where $H_L = Uh/L$ is the hydraulic loading rate of the stream. Equation (3) follows by substituting equations (1a) and (2a).

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Figure Legends:

Fig. 1. Stream physics imposes an upper limit on nitrate uptake by assimilation and denitrification. (**A**) Conceptual model of how nitrate is transported from the bulk stream, across the concentration boundary layer, and into the streambed where it is assimilated and denitrified in the benthic algal layer and hyporheic zone. (**B**) Total uptake velocities (accounting for both nitrate assimilation and denitrification) measured during the LINX II field campaign plotted against mass transfer coefficients calculated from equation (2a). Colors denote surrounding land-use (reference (REF), agriculture (AGR), or urban (URB)). (**C**) Same as (**B**) except denitrification uptake velocities are plotted on the vertical axis. (**D**) Empirical cumulative distributions of total (solid curves) and denitrification (dashed curves) efficiencies by land-use type. Efficiencies were calculated from the ratio of measured uptake velocities and site-specific values of the mass transfer coefficient calculated from equation (2a).

Fig. 2. The upper limit on nitrate uptake is observed in streams with low nitrate concentration. (**A**) The fraction of nitrate removed in the streambed by assimilation and denitrification is negatively correlated with stream nitrate concentration ($r^2 = 0.41, p < 0.01$), and approaches 100% ($\alpha_{\text{tot}} = 1$) when nitrate concentrations are low ($\left[\text{NO}_3^-\right] < 10^{-3}$ mol m^{-3}). (**B**) The fraction of nitrate removed in the streambed by denitrification is also negatively correlated with stream nitrate concentration ($r^2 = 0.32, p < 0.01$). Lines represent least-squares linear regressions of log-transformed efficiency against log-transformed nitrate concentration: $\log_{10}\alpha = a + b\log_{10}\left[\text{NO}_3^-\right]$, where the constants are $a = -2.5 \pm 0.18$ and $b = -0.49 \pm 0.07$ for α_{tot} and $a = -3.36 \pm 0.22$ and $b = -0.49 \pm 0.11$ for α_{tot}.

Fig. 3. A test of the scaling law (equation (3)) derived in this study. (**A**) Empirical cumulative distributions of the observed (symbols) and predicted (curves) fraction of nitrate removed at LINX II sites by both denitrification and assimilation (f_{tot}) or denitrification alone (f_{den}). Predicted values of f_{tot} and f_{den} were calculated from equation (3) after substituting the linear regression models for α_{tot} and α_{den} (see **Fig. 2**) and site-specific values of the shear velocity, stream velocity, reach length, average depth, and stream nitrate concentration (LINX II data tabulated in Supplemental Materials). (**B**) Same data as in (**A**), but plotted so that observed and predicted values of f_{tot} and f_{den} can be compared on a site-by-site basis. The diagonal line represents perfect correspondence.