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NITROGEN CYCLE

Factoring stream turbulence into global assessments of nitrogen pollution

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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 United States concluded that in-stream removal of nitrate is controlled primarily by stream chemistry and biology. Reanalysis of these data reveals that stream turbulence (in particular, turbulent mass transfer across the concentration boundary layer) imposes a previously unrecognized upper limit on the rate at which nitrate is removed from streams. The upper limit closely approximates measured nitrate removal rates in streams with low concentrations of this pollutant, a discovery that should inform stream restoration designs and efforts to assess the effects of nitrogen pollution on receiving water quality and the global nitrogen cycle.

Over the past century, humans have substantially increased nitrogen loading to streams and rivers, primarily from the overapplication 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*–*3*). Thousands of stream, river, lake, groundwater, and coastal sites across the United States are classified as impaired for nitrogen by the U.S. Environmental Protection Agency (*4*). 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 (*5*). 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 (*6*).

Streams have a natural capacity to remove dissolved inorganic nitrogen (DIN, which includes 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 (*7*), a region of the streambed where hydrologic flow paths begin and end in the stream (*8*). 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 dinitrogen (denitrification). Of these reactions, only denitrification permanently removes nitrogen from the stream through the evasion of nitrous oxide or dinitrogen gas. The production of nitrous oxide by streams is responsible for ~10% of global anthropogenic emissions of this potent greenhouse gas (*9*), of which headwater streams may 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 (*10*), whereas the rest is remineralized 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 (*11*). In our study, we focused on nitrate (because of its mobility, recalcitrance, and environmental effects) and quantified its removal with the nitrate uptake velocity $v_f \geq 0$ (units of meters per second), 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 5 years from 2001 to 2006, remains one of the most comprehensive studies of nitrate uptake in headwater streams to date (*7*, *9*, *12*, *13*). LINX II included ^{15}N-labeled nitrate addition experiments in 72 streams across eight regions of the United States, 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). On the basis of 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).

Evaluations of physical controls on nitrate uptake in streams have focused on hyporheic exchange (circulation of water through the hyporheic zone) quantified on the basis of transient storage analysis of conservative tracer injection experiments (*14*) or physical models of water pumping through streambed sediments by static and dynamic pressure variations (*2*, *8*, *15*). Missing from these previous assessments is turbulent mass transport across the concentration boundary layer (CBL) above the streambed. This transport mechanism is a key control on the delivery of oxygen to fine-grained (nonpermeable) sediments (*16*), although its role in mass transfer to coarser (permeable) sediments (like most of the headwater streams included in the LINX II study) is not clear (*17*).

Given the CBL's position between the stream and streambed (Fig. 1A), we hypothesized that nitrate uptake by permeable streambeds might be "bottlenecked" by turbulent transport across the CBL. 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 CBL by turbulence, units of meters per second) 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 that is removed by assimilation and denitrification, unitless) (*18*)

$$v_f = \alpha k_m, v_f \geq 0, 0 \leq \alpha \leq 1, k_m \geq 0 \quad \text{(1A)}$$

$$\alpha = 1 - \frac{1}{\psi + 1}, 0 \leq \psi < \infty \quad \text{(1B)}$$

$$\psi = \frac{v_{bed}}{k_m} \quad \text{(1C)}$$

Conceptually, the mass transfer coefficient k_m represents the potential (mass transfer–limited) uptake velocity of a stream, whereas the efficiency α indicates the fraction of that potential realized in practice. The efficiency depends on a dimensionless number ψ, which represents the balance of nitrate uptake in the streambed (v_{bed}, units of meters per second) and turbulent mass transfer across the CBL. Because efficiency α varies from 0 (ψ→0) to 1 (ψ→∞), if our hypothesis is correct the uptake velocity should always be less than or equal to the mass transfer coefficient: $v_f \leq k_m$ (see Eq. 1A).

As a test of our hypothesis, we estimated values of the mass transfer coefficient at all LINX II sites where uptake velocities were reported for both assimilation and denitrification [total uptake ($v_{f,tot}$), units of meters per second] and denitrification alone [denitrification uptake ($v_{f,den}$), units of meters

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per second] (69 and 49 of the 72 LINX II sites, respectively) (*7*, *12*, *13*). Site-specific values of the transfer coefficient k_m were estimated from surface renewal theory, which assumes that mass transport across the CBL occurs by sweep and ejection events associated with coherent turbulence in the stream, together with molecular diffusion of mass into the streambed (*19*). This theory predicts that k_m can be calculated from routinely measured features of a stream, including slope (S, unitless) and depth (h, units of meters), together with temperature-corrected values for the kinematic viscosity of water (υ, units of square meters per second) and the molecular diffusion coefficient of nitrate in water (D_m, units of square meters per second)

$$k_m = 0.17 u_* \mathrm{Sc}^{-2/3} \quad (2A)$$

$$\mathrm{Sc} = \upsilon / D_m \quad (2B)$$

$$u_* = \sqrt{ghS} \quad (2C)$$

The Schmidt number (Sc, unitless) represents the relative importance of molecular diffusion of momentum and mass, the shear velocity (u_*, units of meters per second) is a measure of stream turbulence, and $g = 9.81$ m s^{-2} is the acceleration of gravity. Very similar formulae for calculating the mass transfer coefficient (Eq. 2A) are obtained for different conceptual models of the sediment-water interface (e.g., rough versus smooth) [reviewed in (*17*)].

With few exceptions and consistent with our hypothesis, the LINX II total and denitrification uptake velocities conform to the inequality $v_f \le k_m$ (Fig. 1, B and C). The implied removal efficiencies (computed from the ratio $\alpha = v_f/k_m$) span approximately three ($10^{-4} < \alpha_{den} < 0.1$) and four ($10^{-4} < \alpha_{tot} \le 1$) orders of magnitude for denitrification and total uptake, respectively (Fig. 1D). The reduced range for α_{den} probably reflects the restrictive nature of denitrification, which requires nitrate to be transported into the streambed (e.g., by hyporheic exchange) and the presence of anoxic conditions and organic carbon, both of which may be rate-limiting in some streams (*10*, *12*, *13*). For the few sites that do not conform to the inequality $v_f \le k_m$, the total uptake velocity exceeds the mass transfer coefficient by factor of 2 or less, well within the uncertainty of the methods used to estimate the mass transfer coefficients (*17*) and uptake velocities (*12*).

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 (Fig. 2). In one of the most notable findings to come out of the LINX II study, a similar negative correlation was observed between nitrate uptake velocity and stream nitrate concentration (*12*). As noted by Mulholland *et al.*, increasing nitrate load to a stream could therefore reduce the nitrate uptake velocity and elicit "a disproportionate increase in the fraction of nitrate that is exported to receiving waters" (*12*). Our hypothesis provides a mechanistic explanation for this key LINX II finding: Uptake velocities are highest in streams with low nitrate concentration because, under such conditions, all nitrate transported to the streambed by turbulence is removed by assimilation and denitrification ($\alpha_{tot} \approx 1$ when $[NO_3^-] < 10^{-3}$ mol m^{-3}) (Fig. 2A), and the nitrate uptake velocity is limited by mass transfer from the stream to the streambed ($v_{f,tot} \approx k_m$). With increasing nitrate concentration, a smaller fraction of nitrate transported to the streambed is removed (α_{tot} declines with increasing $[NO_3^-]$, presumably because sediment-associated autotrophic and heterotrophic organisms are progressively growth-limited by something other than nitrate) and nitrate uptake in the streambed is inefficient ($v_{f,tot} << k_m$). Denitrification efficiencies α_{den} calculated from the LINX II data set follow a similar trend (compare panels A and B in Fig. 2). Across all stream sites sampled in the LINX II study, the denitrification efficiency is a roughly constant fraction of the total efficiency ($\alpha_{den} \approx 0.14\alpha_{tot}$) (*20*).

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 of meters) (*21*)

$$f = 1 - \exp\left[-0.17\alpha\sqrt{\frac{f_D}{8}}\left(\frac{L}{h}\right)\mathrm{Sc}^{-2/3}\right] \quad (3)$$

If the goal is to enhance potential nitrate removal by manipulating stream physics (e.g.,

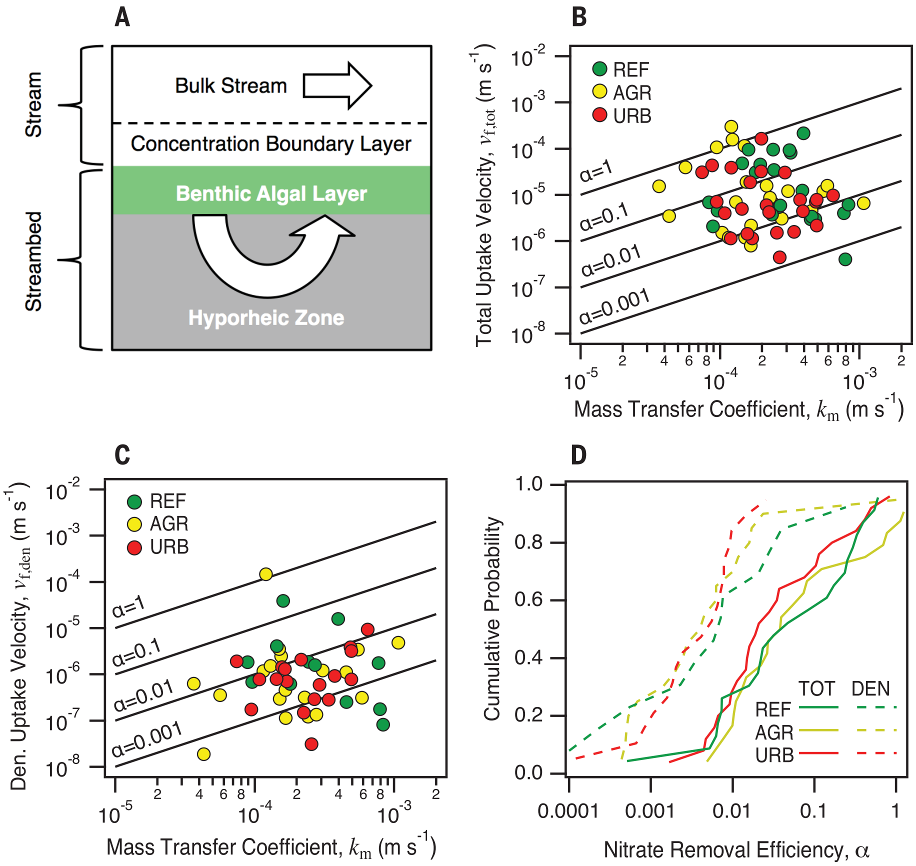

Fig. 1. Stream turbulence imposes an upper limit on nitrate uptake by assimilation and denitrification. (**A**) Conceptual model of how nitrate is transported from the bulk stream, across the concentration boundary layer, and into the streambed where it is assimilated and denitrified in the benthic algal 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 Eq. 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 Eq. 2A.

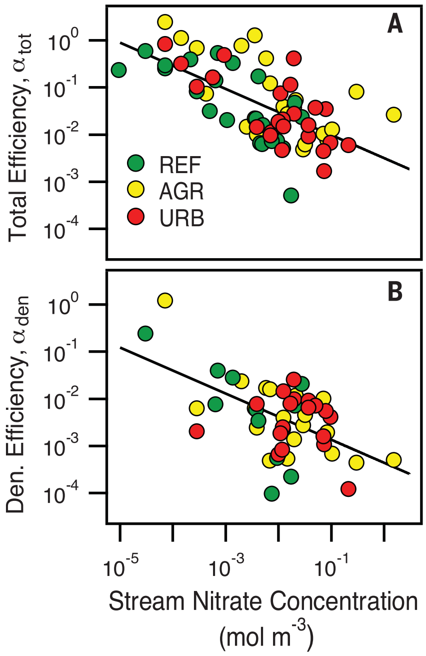

Fig. 2. The turbulence-imposed upper limit on nitrate uptake is observed in streams with low nitrate concentration. (**A**) The fraction of nitrate removed in the streambed by assimilation and denitrification is negatively correlated with stream nitrate concentration (coefficient of determination r^2 = 0.41, P < 0.01) and approaches 100% (α_{tot} = 1) when nitrate concentrations are low ($[NO_3^-] < 10^{-3}$ 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: $\log_{10}\alpha = a + b\log_{10}[NO_3^-]$, 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_{den}.

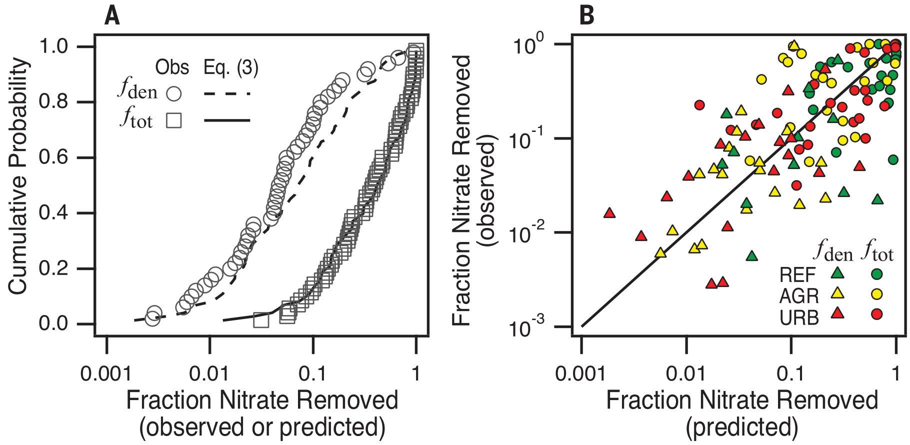

Fig. 3. A test of the scaling law derived in this study. (**A**) Empirical cumulative distributions of the observed (symbols) and predicted (curves) fraction of nitrate removed at LINX II sites by both denitrification and assimilation (f_{tot}) or denitrification alone (f_{den}). Predicted values of f_{tot} and f_{den} were calculated from Eq. 3 after substituting the linear regression models for α_{tot} and α_{den} (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 the supplementary materials). (**B**) Same data as in (A), but plotted so that the observed and predicted values of f_{tot} and f_{den} can be compared on a site-by-site basis. The diagonal line represents a one-to-one relationship.

through stream restoration), Eq. 3 indicates that the Darcy-Weisbach friction factor $f_D = 8u_*^2/U^2$ [where U (units of meters per second) is the average velocity of the stream] and the length-to-depth ratio L/h should be maximized, for instance, using conventional hydraulic relationships (*22*). When stream nitrate concentrations are low (i.e., $[NO_3^-] < 10^{-3}$ 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) (*20*). For stream nitrate concentrations above this threshold, the results in Fig. 2 imply that nitrate uptake is rate-limited by nitrogen cycling and transport within the streambed rather than by turbulent transport of nitrogen from the stream to the streambed. Under these conditions, several options are available for estimating α_{tot} and α_{den}. The simplest involves substituting into Eq. 3 the linear correlations between log-transformed efficiency and log-transformed nitrate (see lines in Fig. 2). When applied to the entire LINX II data set, 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 method also performs poorly when evaluated on a site-by-site basis (Fig. 3B, Nash-Sutcliff efficiency $E = -0.3$ and 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), suggesting that much scope exists for model improvement when $\alpha << 1$. One promising approach along these lines involves coupling surface renewal theory for turbulent mass transport above the streambed with process-based models of nitrogen cycling and transport in the benthic algal layer and hyporheic zone (*18*, *23*, *24*). By incorporating Eq. 3 into stream network models [such as the one recently prepared for the Mississippi River basin (*25*, *26*)], the resulting estimates for α can be scaled up to assess the fate and transport of nitrogen pollution at reach, catchment, continental, and global scales.

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20. The linear regressions presented in Fig. 2 (see legend) can be expressed as $\alpha_{den} = 10^{-3.36}[NO_3^-]^{-0.49}$ and $\alpha_{tot} = 10^{-2.5}[NO_3^-]^{-0.49}$. The claim $\alpha_{den}/\alpha_{tot} \approx 0.14$ follows directly from taking the ratio of these two power laws.
21. We derived Eq. 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 Eqs. 1A and 2A.
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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/359/6381/1266/suppl/DC1
Materials and Methods
Supplementary Text
Table S1
References (*27*–*32*)

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Science

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Stream physics set the limits

A combination of physical transport processes and biologically mediated reactions in streams and their sediments removes dissolved inorganic nitrogen (DIN) from the water. Although stream chemistry and biology have been considered the dominant controls on how quickly DIN is removed, Grant *et al.* show that physics is what sets the limits on removal rates of nitrate (a component of DIN). Residence time in the hyporheic zone (the region below the sediment surface where groundwater and surface water mix) determines the maximum rate at which nitrate can be removed from stream water. Nevertheless, at local scales, chemistry and biology modify how closely to that maximum rate removal occurs.

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