Title
Factoring stream turbulence into global assessments of nitrogen pollution

Permalink
https://escholarship.org/uc/item/8tw3f4rk

Journal
SCIENCE, 359(6381)

ISSN
0036-8075

Authors
Grant, SB
Azizian, M
Cook, P
et al.

Publication Date
2018-03-16

DOI
10.1126/science.aap8074

Supplemental Material
https://escholarship.org/uc/item/8tw3f4rk#supplemental

Peer reviewed
Factoring stream turbulence into global assessments of nitrogen pollution

Stanley B. Grant,1,2,3 Morvarid Azizian,2 Perran Cook,2 Fulvio Boano,4 Megan A. Rippy1

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 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 (1–3). 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 phosphorus 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 streamed 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 streamed 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 $v_{\text{r, tot}}$ (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 15N-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 streamed 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 streamed. 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 streamed (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 $\alpha$ 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)

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

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

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

Conceptually, the mass transfer coefficient $k_m$ represents the potential (mass transfer–limited) uptake velocity of a stream, whereas the efficiency $\alpha$ indicates the fraction of that potential realized in practice. The efficiency depends on a dimensionless number $\psi$, which represents the balance of nitrate uptake in the streamed ($v_{\text{r, bed}}$, units of meters per second) and turbulent mass transfer across the CBL. Because efficiency $\alpha$ varies from 0 ($\psi = \infty$) to 1 ($\psi = 0$), if our hypothesis is correct the uptake velocity should always be less than or equal to the mass transfer coefficient: $v_{\text{r}} \leq k_m$ (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 ($v_{\text{r, tot}}$), units of meters per second] and denitrification alone [denitrification uptake ($v_{\text{r, den}}$), units of meters per second] (18–22).
per second] (69 and 49 of the 72 LINX II sites, respectively) (7, 12, 13). Site-specific values of the mass 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 \((S, \text{ unitless})\) and depth \((h, \text{ units of meters})\), together with temperature-corrected values for the kinematic viscosity of water \((\nu, \text{ units of square meters per second})\) and the molecular diffusion coefficient of nitrate in water \((D_m, \text{ units of square meters per second})\)

\[
k_m = 0.17u_SC^{2/3}
\]

\[
Sc = \frac{u}{D_m}
\]

\[
u_ = \sqrt{ghS}
\]

The Schmidt number \((Sc, \text{ unitless})\) represents the relative importance of molecular diffusion of momentum and mass, the shear velocity \((\nu_\text{, units of meters per second})\) is a measure of stream turbulence, and \(g = 9.81 \text{ m s}^{-2}\) is the acceleration of gravity. Very similar formulae for calculating the mass transfer coefficient \((\text{Eq. 2A})\) 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 \(v_f \leq k_m\) (Fig. 1, B and C). The implied removal efficiencies (computed from the ratio \(a = v_f/k_m\)) span approximately three \((10^{-4} < a_{\text{den}} < 0.1)\) and four \((10^{-2} < a_{\text{tot}} < 1)\) orders of magnitude for denitrification and total uptake, respectively (Fig. 1D). The reduced range for \(a_{\text{den}}\) probably reflects the restrictive nature of denitrification, which requires nitrate to be transported into the streambed \((e.g., \text{by hyporheic exchange})\) 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 \(v_f \leq k_m\) 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 \((\text{Eq. 17})\) and uptake velocities \((\text{Eq. 12})\).

Removal efficiencies calculated from the LINX II data do not exhibit a consistent relationship to catchment land use \((\text{Fig. 1D})\), but they are negatively correlated with stream nitrate concentration \((\text{Fig. 2})\). In one of the most notable findings of the LINX II study, the denitrification efficiency is a roughly constant fraction of the total efficiency \(a_{\text{den}} = 0.14a_{\text{tot}}\) (20).

Our hypothesis also implies a simple scaling relationship for the fraction of nitrate removed \((0 \leq f \leq 1)\) over a stream reach of length \(L\) (units of meters) \((\text{Eq. 21})\)

\[
f = 1 - \exp\left[-0.17\sqrt{\frac{L}{8}} \left(\frac{k_m}{D_m}\right) Sc^{2/3}\right]
\]

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.
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% ($\alpha_{tot} = 1$) when nitrate concentrations are low ([NO$_3$] $< 10^{-3}$ mol m$^{-3}$). 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$_{10}$($\alpha_{tot}$) = a + b log$_{10}$[NO$_3$] where the constants are a = −2.5 ± 0.18 and b = −0.49 ± 0.07 for $\alpha_{tot}$, and a = −3.36 ± 0.22 and b = −0.49 ± 0.11 for $\alpha_{den}$ (through stream restoration).

The Darcy-Weisbach friction factor $f_d$ = $3u^2/2U^2$ [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, in contrast to 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: $\alpha_{tot}$ = 1 and $\alpha_{den}$ = 0.14 (Fig. 2).

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 $\alpha_{tot}$ and $\alpha_{den}$. 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-Sutcliffe 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 $\alpha$ can be scaled up to assess the fate and transport of nitrogen pollution at reach, catchment, continental, and global scales.

**REFERENCES AND NOTES**

18. See supplementary materials for details.
20. The linear regressions presented in Fig. 2 (see legend) can be expressed as $f_{den} = 10^{-3.39}[\text{NO}_3^-]^{−0.49}$ and $f_{tot} = 10^{-3.39}[\text{NO}_3^-]^{−0.49}$.
21. We derived Eq. 3 by performing mass balance over a stream reach, assuming steady uniform flow: $f = 1 − \exp(-UH/h)$, where $H = U/H$ is the hydraulic loading rate of the stream. Equation 3 follows by substituting Eqs. 1a and 2a.

**ACKNOWLEDGMENTS**

We thank M. Gerostek and A. Meiring for valuable feedback and the LINX II researchers for data access. Funding: Financial support was provided by the U.S. NSF Partnerships for International Research and Education (grant OISE-1243543) and the California Office of the President Multicampus Research Program Initiatives (award MRP-17-455083). Author contributions: S.B.G. conceived the study and drafted the article; M.A. curated and analyzed the LINX II data set; F.B. and P.C. contributed text on hyporheic ecosystem processes. Author affiliations: 1. Water Resources and Environmental Engineering Program, University of California—Davis, Davis, California 95616, USA; 2. Earth Sciences and Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA; 3. Water Resources and Environmental Engineering Program, University of California—Davis, Davis, California 95616, USA; 4. Department of Civil and Environmental Engineering, University of California—Davis, Davis, California 95616, USA; 5. Water Resources and Environmental Engineering Program, University of California—Davis, Davis, California 95616, USA. Competing interests: None declared. Data and materials availability: The supplementary materials include a derivation of Eq. 1, data reduction methods, an example of how the theory presented here can be coupled to process-based models of nitrogen cycling and transport in the hyporheic zone, and a compilation of the LINX II data used in this study.

**SUPPLEMENTAL MATERIALS**

www.sciencemag.org/content/359/6381/1266/suppl/DC1

**AUTHOR CONTRIBUTIONS**

S.B.G. conceived the article. All authors provided edits.

**ADDITIONAL MATERIALS**

Table S1 References (27–32)

29 August 2017; accepted 31 January 2018
10.1126/science.aap7074
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. Science, this issue p. 1266