WebPanel 1. A model for scaling denitrification to river networks

We developed a model of NO_3^- loading, transport, and denitrification in stream and river networks (described in detail by Mulholland *et al.* 2008) to scale up empirical measures of stream-reach denitrification. The model is based on a steady-state, mass-balance approach and hydrogeomorphic scaling principles commonly used to represent river geomorphology and hydrology, including: (1) steady-state hydrologic flux; (2) accumulation of water in streams and rivers from their drainage areas as they flow downstream; (3) uniform water yield for each sampled subcatchment (see Figure 2); and (4) channel width increasing downstream in proportion to discharge. In accordance with typical river-network model assumptions, denitrification is the primary nitrogen removal pathway (Wollheim *et al.* 2006).

The model calculates denitrification within stream segments and routes water (Q; $m^3\ d^{-1}$) and NO_3^- ($NO3$; $g\ d^{-1}$) between segments linked together into networks (see Figure 1). Upstream inputs to a stream segment (i) of water (Q_{ui}) and NO_3^- ($NO3_{ui}$) are equal to the sum of exports from upstream segments.

$Q_{ui} = \Sigma(Q_{i-1})$ (Eq 1) $\qquad NO3_{ui} = \Sigma(NO3_{i-1})$ (Eq 2)

Lateral water (Q_{Li}) and NO_3^- ($NO3_{Li}$) inputs from the terrestrial landscape are equal to the product of the area draining directly to stream segment i (A, m^2) and the area specific loading rate (Y) of water ($m^3\ m^{-2}\ d^{-1}$) and NO_3^- ($kg\ m^{-2}\ d^{-1}$).

$Q_{Li} = A_i Y_{Qi}$ (Eq 3) $\qquad NO3_{Li} = A_i Y_{NO3i}$ (Eq 4)

We calculated downstream exports using a steady-state mass-balance approach where downstream fluxes of water (Q_{ei}) and NO_3^- ($NO3_{ei}$) equal the sum of inputs minus outputs.

$Q_{ei} = Q_{ui} + Q_{Li}$ (Eq 5) $\qquad NO3_{ei} = NO3_{ui} + NO3_{Li} - NO3_{Ri}$ (Eq 6)

$NO3_{Ri}$ is the NO_3^- removed from stream segment i via denitrification, and is the product of the fraction of NO_3^- denitrified (R) and the sum of NO_3^- inputs to the segment.

$NO3_{Ri} = R_i(NO3_{ui} + NO3_{Li})$ (Eq 7)

The fraction of NO_3^- denitrified from each stream segment is determined by:

$R = 1 - e^{-\upsilon_{fden}/H_L}$ (Eq 8)

where hydraulic load (H_L, $m\ s^{-1}$) is the ratio of discharge to streambed surface area (length times width of each stream segment; Wollheim *et al.* 2006). Stream length was determined from USGS stream hydrography data (1:24 000). Stream width (w) was calculated using modeled discharge (Q) for each stream segment (Leopold and Maddock 1953):

$w = aQ^b$ (Eq 9)

Parameters a and b were estimated empirically for low-flow conditions within each catchment (WebTable 1). Because water yields and width parameters were derived from low-flow measurements, the model scenarios apply to low-flow conditions within each catchment.

Conceptually, uptake velocity for denitrification (υ_{fden}) is the downward velocity of NO_3^- molecules through the water column necessary to meet observed streambed denitrification demand for NO_3^-. Mulholland *et al.* (2008) demonstrated that υ_{fden} decreases with increasing in-stream NO_3^- concentration ($[NO3]$), following a power function. Thus, the model determines υ_{fden} for each stream segment according to:

$\upsilon_{fden} = c\,[NO3]^d$ (Eq 10)

We derived parameters c and d empirically for each catchment using observed values of υ_{fden} and $[NO3]$ from 5–9 experimental stream reaches located within or adjacent to each modeled network (WebTable 1).

WebTable 1. Site-specific parameter values for river-network modeling

Site abbreviation	*Channel width a, b (r^2)*	*Uptake velocity (υ_{fden}) c, d (r^2)*
NC	7.3, 0.45 (0.90)	8.2E-1, –1.2 (0.72)
KS	7.2, 0.35 (0.74)	2.3E-4, –0.48 (0.61)
OR	7.2, 0.35 (0.74)	7.6E-1, –1.2 (0.18)
WY	7.0, 0.33 (0.50)	8.5E-1, –0.10 (0.88)
MA	7.4, 0.27 (0.37)	4.0E-4, –0.47 (0.60)
MI	10.4, 0.45 (0.93)	1.1E-1, –0.93 (0.53)
PR	6.6, 0.35 (0.27)	3.4E-6, –0.063 (0.01)
NM	nd	4.2E-5, –0.36 (0.23)

Notes: The width coefficient (a) and exponent (b) were used to determine channel width for each stream segment (using Eq 9 in WebPanel 1). The denitrification coefficient (c) and exponent (d) were used to determine denitrification uptake velocity (υ_{fden}) for each stream segment (using Eq 10 in WebPanel 1). nd = no data.

WebTable 2. Literature review used to determine the realistic range of modeled NO_3^- loading estimates

Location	*Number of catchments*	*Catchment area (km^2)*	*% agriculture*	*% urban*	*Loading estimate (kg N km^{-2} d^{-1})*	*Method used to estimate loading*	*Reference*
Loch Vale Watershed, Colorado Front Range	1	6.6	0	0	0.69	Modeled direct total N loading to aquatic ecosystems	Baron and Campbell (1997)
Upper Mississippi	3	492 000 (422 000–1 320 000)	nd	nd	1.93 (0.28–2.52)	Measured NO_3^- river export	Carey *et al.* (2001)
Embarrass River, Illinois	1	482	91	4.5	6.54	Measured NO_3^- river export	David *et al.* (1997)
Gwynns Falls, Maryland	3	0.32 (0.08–0.81)	0 (0–100)	0 (0–47)	1.78 (0.14–4.49)	Measured total N river export	Groffman *et al.* (2004)
Lake Michigan basin	18	2398 (153–15 825)	42 (5–82)	2 (0.2–20)	0.86 (0.47–3.63)	Measured total N river export	Han *et al.* (2009)
Southeast US	14	2125 (63–56 894)	16 (2–42)	0.5 (0.05–5)	1.30 (0.71–2.50)	Measured total N river export	Harned *et al.* (2004)
LTER sites across North America	13	0.38 (0.06–10)	nd	nd	0.19 (0.03–1.18)	Measured dissolved inorganic N river export	Kane *et al.* (2008)
Oldman River, Alberta, Canada	1	28 200	nd	nd	0.76	Measured total N river export	Rock and Mayer (2006)
US West Coast	18	8995 (1531–279 438)	6 (0.4–24)	1 (0–20)	0.32 (0.19–4.57)	Measured total N river export	Schaefer *et al.* (2009)
Sierra Nevada and Rocky Mountains	28	1.6 (0.2–19.1)	nd	nd	0.20 (0.008–0.85)	Measured dissolved inorganic N river export	Sickman *et al.* (2002)
Central Valley, California	23	2736 (461–61 721)	6 (0–74)	2 (0–6)	0.31 (0.06–2.59)	Measured total N river export	Sobota *et al.* (2009)
Northeast US	16	11 945 (475–70 189)	10 (1–61)	3 (0– 22)	5.51 (2.74–6.96)	Modeled estimates of NO_3^- leaching to ground and surface waters	Van Breeman *et al.* (2002)
Ipswich River basin, Massachusetts	1	404	7	35	1.85	Estimated direct total N loading to river network by 1st-order streams	Williams *et al.* (2004)
Summary	140	1791 (0.06–1 320 000)	10 (0–100)	1.2 (0–47)	0.49 (0.008–6.96)		

Notes: Catchments in the literature review span a wide range of geographic regions, catchment areas, and land-use conditions. When references included more than 1 year of loading data for a particular catchment, the average value was used. Data are reported as median (range). The highest reported nitrogen loading rate was 6.96 kg N km^{-2} d^{-1}. nd = no data.

WebReferences

Baron JS and Campbell DH. 1997. Nitrogen fluxes in a high elevation Colorado Rocky Mountain basin. *Hydrol Process* **11**: 783–99.

Carey AE, Lyons WB, Bonzongo JC, and Jehrter JC. 2001. Nitrogen budget in the Upper Mississippi River watershed. *Environ Eng Geosci* **7**: 251–65.

David MB, Gentry LE, Kovacic DA, and Smith KM 1997. Nitrogen balance in and export from an agricultural watershed. *J Environ Qual* **26**: 1038–48.

Groffman PM, Law NL, Belt KT, *et al.* 2004. Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems* **7**: 393–403.

Han H, Allan JC, and Scavia D. 2009. Influence of climate and human activities on the relationship between watershed nitrogen input and river export. *Environ Sci Technol* **43**: 1916–22.

Harned DA, Atkins JB, and Harvill JS. 2004. Nutrient mass balance and trends, Mobile River Basin, Alabama, Georgia and Mississippi. *J Am Water Resour As* **40**: 765–93.

Kane ES, Betts EF, Burgin AJ, *et al.* 2008. Precipitation control over inorganic nitrogen import–export budgets across watersheds: a synthesis of long-term ecological research. *Ecohydrol* **1**: 105–17.

Leopold LB and Maddock T. 1953. The hydraulic geometry of streams and some physiographic implications. US Geological Survey Professional Paper 252. Washington, DC: United States Government Printing Office.

Mulholland PJ, Helton AM, Poole GC, *et al.* 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature* **452**: 202–46.

Rock L and Mayer B. 2006. Nitrogen budget for the Oldman River Basin, southern Alberta, Canada. *Nutr Cycl Agroecosyst* **75**: 147–62.

Schaefer SC, Hollibaugh JT, and Alber M. 2009. Watershed nitrogen input and riverine export on the west coast of the US. *Biogeochemistry* **93**: 219–33.

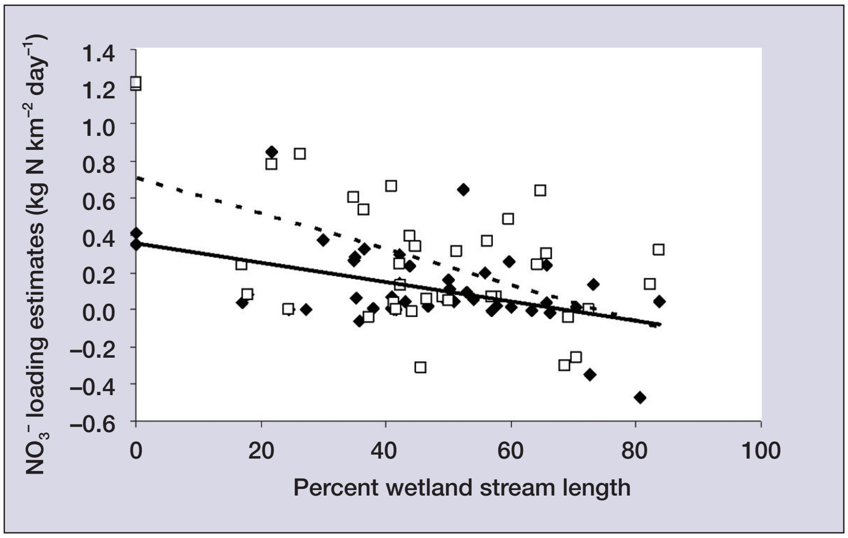
Sickman JO, Melack JM, and Stoddard JL. 2002. Regional analysis of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains. *Biogeochemistry* **57**: 341–74.

Sobota DJ, Harrison JA, and Dahlgren RA. 2009. Influences of climate, hydrology, and land use on input and export of nitrogen in California watersheds. *Biogeochemistry* **94**: 43–62.

Van Breemen N, Boyer EW, and Goodale CL. 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. *Biogeochemistry* **57**: 267–93.

Williams M, Hopkinson C, Rastetter E, and Vallino J. 2004. N budgets and aquatic uptake in the Ipswich River basin, northeastern Massachusetts. *Water Resour Res* **20**; doi: 10.1029/2004WR003172.

Wollheim WM, Vorosmarty CJ, Peterson BJ, *et al.* 2006. Relationship between river size and nutrient removal. *Geophys Res Lett* **33**; doi:10.1029/2006GL025845.



WebFigure 1. *Modeled NO_3^- loading estimates from the Ipswich River, MA, versus upstream percent wetland stream length (ie ratio of stream length passing through wetlands to total stream length). Wetland extent determined from 2001 National Land Cover Dataset (http://seamless.usgs.gov). Loading estimates derived from network modeling were negatively correlated with percent wetland stream length for both years of estimated loading rates (2003 $r^2 = 0.21$, $P < 0.002$, solid line and diamonds and 2004 $r^2 = 0.31$, $P < 0.002$, dashed line and open squares), suggesting that the model underpredicts denitrification in channels flowing through wetlands.*