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Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate

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The flux of nitrogen (N) to coastal marine ecosystems is strongly correlated with the "net anthropogenic nitrogen inputs" (NANI) to the landscape across 154 watersheds, ranging in size from 16 km^2 to 279 000 km^2, in the US and Europe. When NANI values are greater than 1070 kg N km^{-2} yr^{-1}, an average of 25% of the NANI is exported from those watersheds in rivers. Our analysis suggests a possible threshold at lower NANI levels, with a smaller fraction exported when NANI values are below 1070 kg N km^{-2} yr^{-1}. Synthetic fertilizer is the largest portion of NANI in many watersheds, but other inputs also contribute substantially to the N fluxes; in some regions, atmospheric deposition of N is the major component. The flux of N to coastal areas is controlled in part by climate, and a higher percentage of NANI is exported in rivers, from watersheds that have higher freshwater discharge.

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Excessive amounts of nitrogen (N) represent the largest pollution problem in coastal marine waters. Human activity has increased N inputs by 10- to 15-fold in many regions, but has had little effect in others (NRC 2000; Howarth *et al.* 2005, 2011). Nitrogen derives from many sources, and different sources of N dominate in different areas. Twenty years ago, Peierls *et al.* (1991) demonstrated a correlation between human population density and nitrate fluxes in very large rivers and suggested that sewage was the primary cause, with perhaps a contribution from atmospheric deposition. At the coarse scale, Peierls *et al.* (1991) analyzed drivers – including fertilizers and other agricultural inputs – could not be discerned. Today, the relative contribution of sources to coastal N pollution remains uncertain in many cases, in part because no direct approaches for making such evaluations exist. In such instances, models provide the only robust assessment tool (EPA–SAB 2008).

In a nutshell:

- Nitrogen (N) pollution is one of the primary threats to the ecological integrity of estuaries and other coastal marine ecosystems
- Although synthetic fertilizer is the main source of N pollution in many areas, other sources – such as atmospheric deposition and the movement of N in food and animal feeds – contribute, and are sometimes dominant
- N fluxes in rivers to coastal ecosystems increase as the "net anthropogenic nitrogen inputs" (NANI) to the landscape increase
- NANI provides a powerful approach for estimating these N fluxes and for determining the major sources of N pollution in the landscape

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In one paper from a 1994 workshop, Howarth *et al.* (1996) examined the flux of N from large watershed regions to the North Atlantic Ocean in the context of the N inputs to the landscape from human activity. Inputs considered were use of synthetic N fertilizer, N fixation associated with agricultural crops, atmospheric deposition of oxidized N (NO_y), and the net movement of N into or out of the region in human food and animal feeds. We termed the sum of these inputs the "net anthropogenic nitrogen inputs", or NANI. At the coarse scale of large regions surrounding the North Atlantic Ocean, the average multiyear flux of N transported in rivers to the North Atlantic was well correlated with NANI. Alexander *et al.* (2002) compared many models for estimating N fluxes in large river basins and concluded that a simple model that predicts N flux as a linear function of NANI was one of the most accurate, with low bias and error as compared with those of more complicated models. This simple model has since been used to estimate the total riverine N flux from the global landscape to the world's oceans (Galloway *et al.* 2004; Boyer *et al.* 2006).

NANI does not include sewage or animal wastes because these are simply flows of N that originate from other sources already included in NANI. Similarly, the only atmospheric input considered is NO_y deposition, which in the temperate zone originates largely from fossil-fuel combustion and is therefore a new input of N to the

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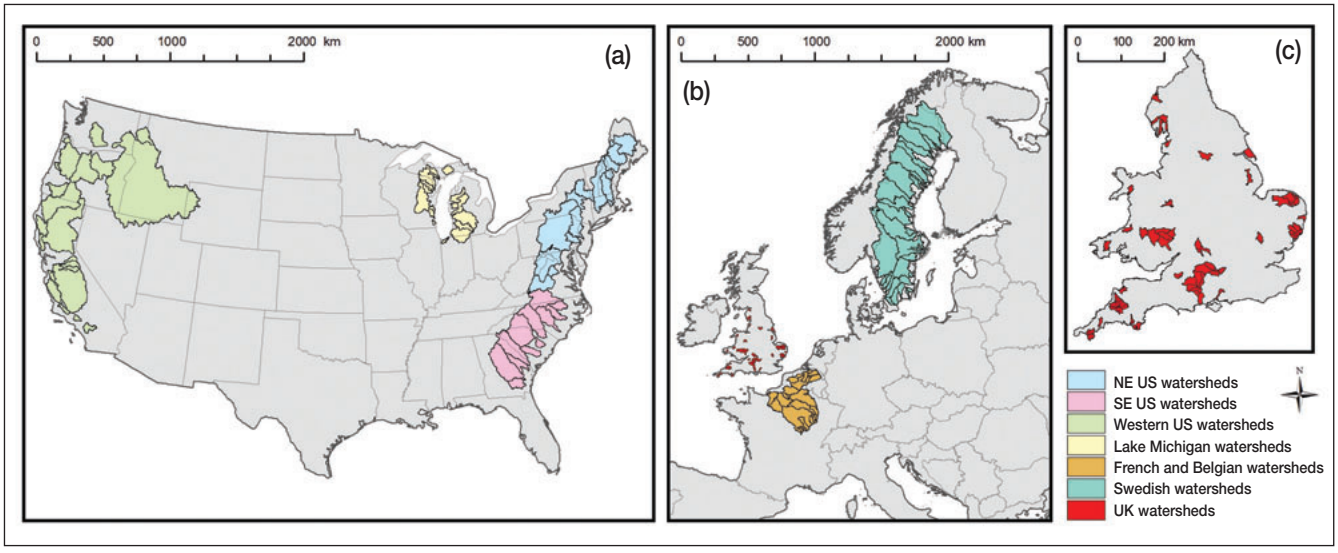

Figure 1. *Maps showing the distribution of the watersheds included in our analysis (a) in the US and (b) in Europe. The watersheds in the UK are shown both in the European map and (c) in the more detailed map of the UK.*

landscape. Deposition of ammonia is excluded, given that most of the ammonia in the atmosphere is deposited near the site of emission to the atmosphere (ie within the same region) and originates from agricultural sources already included in NANI (Howarth *et al.* 1996, 2006).

The NANI approach, or the closely related approach of considering total N inputs (TNI, which is equivalent to NANI plus natural N fixation), has been applied in many regions, including the northeastern US (Alexander *et al.* 2002; Boyer *et al.* 2002; Howarth *et al.* 2006), the southeastern US (Schaefer and Alber 2007), many of the watersheds on the west coast of the US (Schaefer *et al.* 2009), and watersheds in Michigan (Han and Allan 2008). In all of these cases, riverine N fluxes were well correlated with NANI (or TNI), but the percentage of the N inputs exported in rivers varied among the regions. Several of these previous studies suggested that the fraction of NANI exported in riverine flows is related to climatic variables, including precipitation, temperature, and freshwater discharge. However, these studies' conclusions often contradicted one another. We hypothesized that the influence of climate on the relationship of NANI and riverine N flux might become clearer if a larger set of watersheds from a diversity of regions were considered. Here, we report on such a study, one that includes 154 US and European watersheds.

Data sources

Our analysis included watersheds in the US, France, Belgium, the UK, and Sweden (Figure 1). The watersheds varied considerably in size, from 16 km^2 to 279 000 km^2. The US watersheds included 16 in the northeast (Boyer *et al.* 2002; Howarth *et al.* 2006), 12 in the southeast (Schaefer and Alber 2007), 17 in the west (Schaefer *et al.* 2009), and 18 in the upper midwest (Han and Allan 2008). For the US watersheds, we used published data (Howarth *et al.* 2006; Schaefer and Alber 2007; Schaefer *et al.* 2009; Han and Allan 2008) for estimates of area, average discharge, average temperature, and riverine total nitrogen flux (see WebTable 1), and for 3 out of 4 of the input terms for NANI: synthetic fertilizer, nitrogen fixation in agroecosystems, and the net input of nitrogen in human food and animal feeds. These data generally come from the county scale. To estimate the fourth input term – NO_y deposition – we used output from the US Environmental Protection Agency's Community Multiscale Air Quality (CMAQ) system rather than the NOy deposition estimates reported in the original papers. CMAQ is an emission-based model that predicts total oxidized deposition, including gases across the US, at a grid of 36 km × 36 km (www.cmaq-model.org/).

The European watersheds included 25 in France and Belgium, 30 in the UK, and 36 in Sweden (WebTable 1). The French and Belgian basins included the Seine, Somme, and Scheldt watersheds and 22 nested subbasins; these basins and the approach used for estimating the NANI terms are described in Billen *et al.* (2009). The NANI budgets for the UK watersheds were constructed through government (Department for Environment, Food and Rural Affairs) statistics on food and feed import/export for the UK, and UN Food and Agriculture Organization (FAO) and UK statistics on precipitation, discharge, climatic variables, riverine N flux, and the N content of food and feed consumed in the UK, following the approach outlined by Boyer *et al.* (2002). Background data for the UK watersheds were derived from a range of sources, including research reports for the UK Environment Agency, and published studies (see WebReferences). For all Swedish watersheds, we used agricultural statistics obtained from the Statistiska-Centralbyrån for 1995 (www.scb.se). We constructed food and feed budgets following Boyer *et al.* (2002), using the statistical agricultural data together with FAO statistics. Fertilizer

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use data were obtained from Eurostat (http://epp.eurostat.ec.europa.eu/). Riverine N flux, climatic, and atmospheric deposition data were collected from the Baltic Environmental Database (http://nest.su.se/models/bed.htm). For all the European watersheds, we derived deposition estimates from the European Monitoring and Evaluation Programme's model, an emissions-based model similar to CMAQ, using a grid of 50 km × 50 km. For the other NANI terms, estimates were generally based on the finest scale of administrative government unit for which information was available, roughly equivalent to county-scale data in the US.

For all watersheds included in this paper, the riverine N fluxes reported are multi-year averages, usually for 6 or 7 years. The NANI estimates come from a single-year period within those 6 or 7 years. Note that NANI generally does not vary greatly over short time intervals (Hong *et al.* 2011).

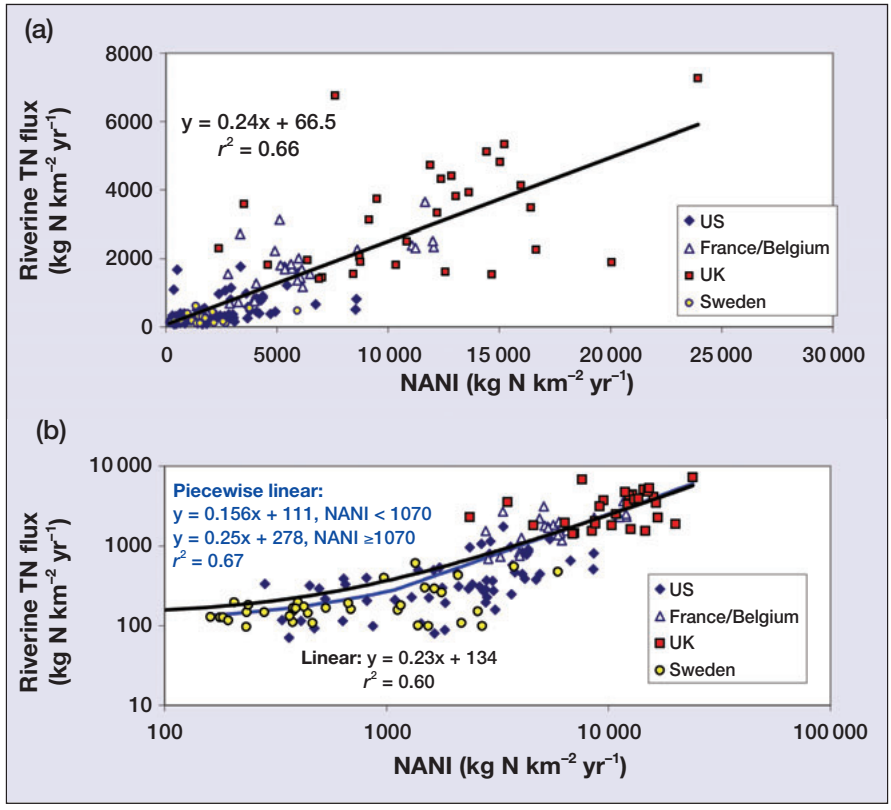

Figure 2. *The flux of N from the landscape in rivers is significantly and highly correlated with NANI on both (a) linear (P = 2 × 10^{-37}) and (b) log–log (P = 3 × 10^{-32}) scales across the 154 watersheds. In the log–log plot, we explored a possible threshold break point in the function, fitting two line segments with the break point determined by minimizing the sum of squared deviations using the Solver add-on in Microsoft Excel. This piecewise linear fit suggests a threshold response at a NANI value of approximately 1070 kg N km^{-2} yr^{-1}, with the slope of the line above this threshold being virtually the same as for the linear fit in (a). The slopes of these relationships indicate that, on average, approximately 25% of NANI is exported from the landscape to coastal oceans, at least for the values of NANI greater than 1070 kg N km^{-2} yr^{-1}.*

Riverine N flows and NANI

Riverine N flux from the 154 watersheds is significantly correlated with NANI on both linear and log–log scales (Figure 2, a and b). The slope of the regression on the linear scale (Figure 2a) indicates that, on average, approximately 25% of NANI is exported in the rivers included in this study. The slope for the single-line fit in the log–log plot is less, but we also explored a threshold response in the log–log relationship by using a piecewise linear fit. The existence of a threshold might indicate some saturation process at the watershed scale, as was previously observed at smaller scales for inputs of N from atmospheric deposition to forests (Aber *et al.* – 2003) and for fertilizer inputs to agroecosystems (Howarth *et al.* 2005; Billen *et al.* 2007). The piecewise linear fit to the log–log relationship suggests a threshold response at a NANI value of approximately 1070 kg N km^{-2} yr^{-1}, with the slope of the line above this threshold being virtually the same as for the linear fit in Figure 2a and indicating that 25% of NANI is exported in rivers. At lower levels of NANI, the percentage of NANI exported appears to be less than 25%.

The fate of NANI that is not exported in rivers – some 75% on average at higher NANI levels – remains poorly known. For the northeastern US, the best available evidence suggests that some is retained in soils and forest biomass, but more is denitrified (van Breemen *et al.* 2002). A better understanding of the fate of non-river-exported NANI is critical if we are to predict how sinks and fluxes may change in the future as a result of climate change, land-use change, and saturation of some sinks.

The NANI approach was originally developed for very large regions (such as the entire northeastern US from Maine through Virginia, or the entire Mississippi River basin), and has subsequently been applied to smaller – but generally still large – watersheds (Alexander *et al.* 2002; Howarth *et al.* 2006; Schaefer and Alber 2007; Han and Allan 2008; Schaefer *et al.* 2009). For several reasons, one might expect the approach to be more robust at larger spatial scales and to break down below some threshold watershed size. For example, cross-boundary transfer of ammonia in the atmosphere is small relative to other NANI terms at large spatial scales but becomes increasingly important at smaller scales (Howarth *et al.* 2006). Also, the NANI approach is presumably most robust when watersheds are large relative to the scale of input data. For NO_y deposition in the US, this spatial scale for input data is 1296 km^2, and for some other data in

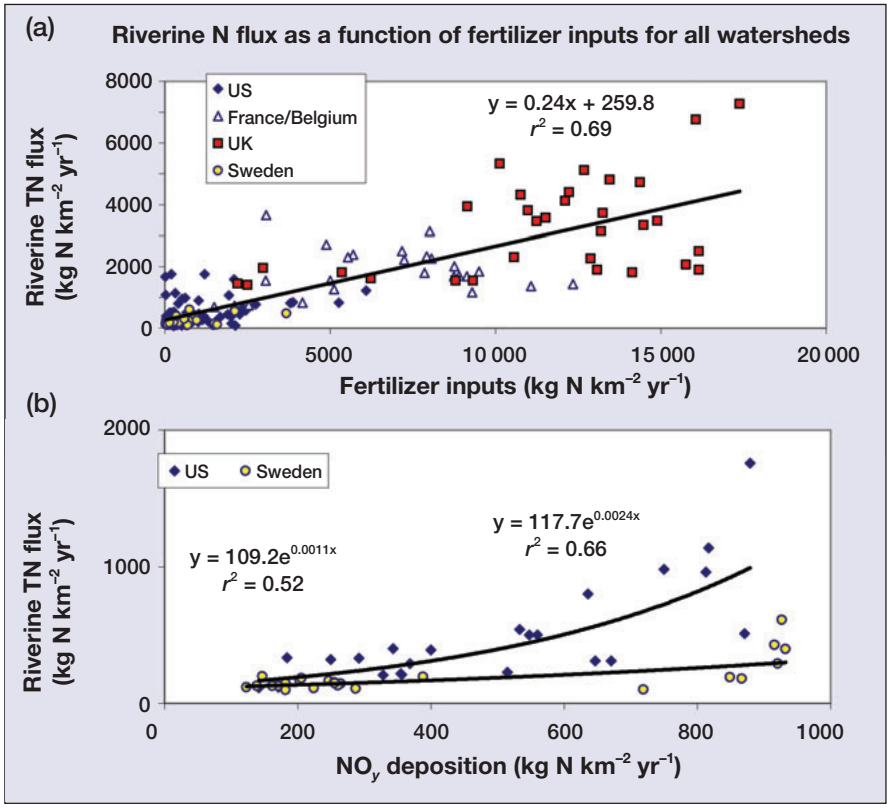

Figure 3. *(a) Synthetic N fertilizer is often the major term of NANI in watersheds, and fertilizer alone is significantly correlated with the average flux of N in rivers across the 154 watersheds* ($P = 5 \times 10^{-41}$)*. (b) The atmospheric deposition of oxidized N* (NO_y) *is an important term of NANI in some watersheds; for those watersheds where this deposition equals or exceeds the input of synthetic N fertilizer, deposition is significantly correlated with riverine N fluxes* ($P = 2 \times 10^{-16}$ *for the US watersheds and* [$P = 7 \times 10^{-5}$] *for the Swedish watersheds). Note that the N in* NO_y *deposition originates largely from the combustion of fossil fuels, and also contributes to acid rain.*

various locations, the scale is even coarser. We searched for a size-threshold effect on the utility of the NANI approach by analyzing the goodness of fit between NANI and riverine N flow while step-wise deleting one watershed at a time from the analysis by dropping the smallest remaining watershed at each step (WebFigure 1). The goodness of fit in the relationship gradually improved as watersheds were deleted, but in general we saw few if any sharp break points. This suggests that the NANI approach is reasonably robust and predictive, even in watersheds that are far smaller than those to which the approach has usually been applied in the past. For many of the analyses in this paper, we concentrate on watersheds greater than 250 km^2. These analyses often show similar statistical results when cutoffs of 250 km^2, 500 km^2, or 1000 km^2 are used, but far less statistically powerful results when watersheds smaller than 250 km^2 are included.

We also explored incorporating TNI by adding the natural rate of N fixation to NANI. The TNI approach is conceptually attractive, because the mass balance for N input terms is more complete (Boyer *et al.* 2002). However, N fixation is difficult to measure, and data for particular regions or watersheds are seldom available. Even when such data are available, they are difficult to extrapolate to the watershed scale. We estimated the natural rate of N fixation from the regression between evapotranspiration and fixation developed by Cleveland *et al.* (1999) for a global dataset on N fixation. Evapotranspiration for our watersheds was estimated as the difference between precipitation and freshwater discharge. Riverine N fluxes from the watersheds are significantly correlated with both TNI and NANI (WebFigure 2). The two relationships are extremely similar, and a test of coincidence of the regressions shows no significant differences between the two. Given that the TNI approach requires the estimation of a highly uncertain term (ie the natural rate of N fixation) and does not significantly improve the correlation with riverine N flux, we prefer the NANI approach.

The influence of the individual NANI terms

Each NANI component contributes to riverine N flux. For many of the watersheds included here, synthetic N fertilizer is the single largest input. Not surprisingly, therefore, fertilizer input alone is significantly correlated with riverine N flux (Figure 3a). More surprising is the finding that agricultural N fixation alone (WebFigure 3) and NO_y deposition alone (WebFigure 4) are also correlated with riverine N flux. The contribution of atmospheric deposition holds for the entire dataset but becomes quite notable when looking at the subset of watersheds for which NO_y deposition is greater than fertilizer inputs (Figure 3b). This group only includes watersheds in the US and in Sweden; we have fit separate regressions for the watersheds in the two countries. Both show an exponential response with proportionately greater N flux in rivers as deposition increases above 500–900 kg N km^{-2} yr^{-1}. This is consistent with the threshold for downstream leakage of N from forests receiving atmospheric deposition as described in Aber *et al.* (2003). However, unlike the forests studied by Aber *et al.* (2003), the watersheds in our analysis receive other NANI components. The higher riverine N flux for a given input of N deposition in the US as compared with that in Sweden is probably the result of these other NANI components being greater in the US watersheds (WebTable 1).

The net input of N in food and animal feeds has two

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relationships with river N flux. This net input is positively correlated with riverine N flux when the net food and feed term is positive, and is negatively correlated with riverine N flux when the net food and feed term is negative (Figure 4). The positive correlation for positive net inputs in food and feed is driven by sewage and animal wastes from the imported food and feeds. The watersheds that have large net negative inputs of N in food and feeds (ie positive net exports) are agricultural regions that export crop products. In these, the export of food and feed is supported by large inputs of synthetic N fertilizer and/or N fixation. Indeed, over the entire dataset of 154 watersheds, the net food/feed term is negatively correlated with the sum of fertilizer and agricultural N fixation (WebFigure 5). Thus, the negative correlation of the net food/feed term with riverine N flux is clearly driven by fertilizer use and N fixation.

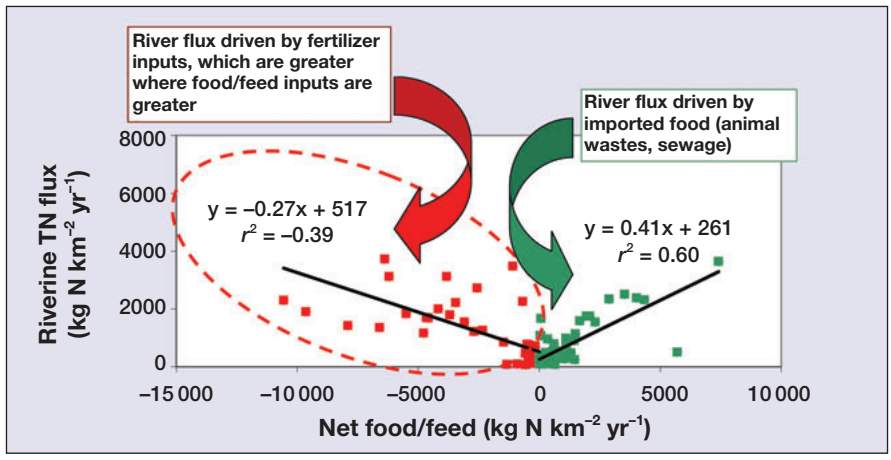

Figure 4. *The net input of N in food for humans and in animal feeds has a complex relationship with the flux of N in rivers, shown here for watersheds that are larger than 250 km^2. For those watersheds with a positive net input of N in food and feed (ie a net import of food and feeds; green squares), the flux of N in rivers increases as the net import increases. This presumably reflects the influence of animal wastes and human sewage. For those watersheds with a negative net input of N in food and feed (ie a net export of food and feeds; red squares), the riverine N flux increases as the net import of food and feed becomes more negative (ie the basin exports more). This is probably due to much greater input of synthetic N fertilizer in the watersheds with the greater export of food and feed. Both of the relationships shown are highly significant:* $P = 1 \times 10^{-14}$ *for the green squares and* $P = 6 \times 10^{-8}$ *for the red squares.*

The role of climate

In an earlier paper that looked at only 16 northeastern US watersheds, the fraction of NANI exported in rivers was clearly correlated with precipitation and discharge but not with temperature (Howarth *et al.* 2006). For a similar analysis that included both northeastern and southeastern US watersheds, Schaefer and Alber (2007) found that the fraction of NANI exported was correlated with all of these climate variables, but suggested that temperature had the strongest relationship. Conversely, Schaefer *et al.* (2009) found no relationship between the fraction of NANI exported and any climate variable in the western US.

The riverine N flux data in this paper and in Howarth *et al.* (2006), Schaefer and Alber (2007), and Schaefer *et al.* (2009) are all averages for multiple years. Other studies have demonstrated that when examining year-by-year patterns, the fraction of NANI exported is greater in years with high discharge and less in years with low discharge, but this can be explained as storage of N in the landscape in dry years followed by flushing in wet years (McIsaac *et al.* 2001; Donner and Scavia 2007; Han *et al.* 2009; David *et al.* 2010). For watersheds with low inputs of anthropogenic N, long-term average riverine N fluxes are greater in those having higher discharge, but this may be the result of differences in rates of natural N fixation (Lewis *et al.* 1999; Lewis 2002; Howarth *et al.* 2006).

Here, we return to the question raised in Howarth *et al.* (2006): is there an influence of climate on the long-term average riverine N flux that is related to the long-term sinks in the landscape, which are primarily denitrification and accumulation of N in soils and biomass (van Breemen *et al.* 2002)? That is, with the larger dataset now available, is there an influence of climate on the average amount of NANI exported over multiple-year periods aside from interannual storage and flushing? The answer is yes: the fraction of NANI exported in long-term average riverine N flux is significantly correlated with temperature, precipitation, and discharge (WebFigure 6). The explanatory power of the relationships is weak for both temperature and precipitation (r^2 = 0.03 and 0.11; P = 0.037 and 9×10^{-5}, respectively). However, discharge is highly correlated with the fraction of NANI exported in rivers (r^2 = 0.41, $P = 5 \times 10^{-16}$; WebFigure 6).

One might question whether the relationship between the fraction of NANI exported and discharge is a result of auto-correlation, because discharge information is used to estimate riverine N flux. The same question can be raised about studies that demonstrate an influence of discharge on long-term average N flux from watersheds with low human impact (Lewis *et al.* 1999; Lewis 2002) or that show the relationship of interannual N flux to discharge (McIsaac *et al.* 1999; Donner and Scavia 2007; Han *et al.* 2009; David *et al.* 2010). In fact, this is not of concern, because the discharge information used to estimate riverine N fluxes is taken at short time intervals and multiplied by the N concentration over the same time interval. The N concentration generally is not a simple function of this short time discharge, and concentrations can be higher or lower at different discharge rates, with different

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trends in different systems (McDiffett *et al.* 1989; Bachman *et al.* 2002). Although annual average discharge itself is indeed correlated with riverine N flux across the watersheds in this study (P = 0.007 for the slope; WebFigure 7), the relationship has rather little explanatory power (r^2 = 0.056). In part this is because of the human domination of the N cycle, which is captured in NANI. Discharge better explains the fraction of NANI exported (WebFigure 6) than riverine N flux (WebFigure 7).

We used a multiple regression approach to explore the influence of climate on N fluxes in rivers, excluding small watersheds (< 250 km^2; WebTable 2). We tested models to estimate the riverine N flux based on various functions of NANI, discharge, and temperature, as well as models that either did or did not force the intercept through zero. We followed the guidance of Hirsch *et al.* (1993) and only tested simple regression models based on physically plausible explanations for relating the climate variable to riverine N flow. The intercept term was never significant in these models, and here we show only the models with the zero intercept. Temperature alone as a term was never significant (WebTable 2). On the other hand, NANI terms were always significant, as were NANI-discharge interaction terms. The most parsimonious of these models is based on a NANI term and a separate NANI-discharge interaction term, with both being highly significant: predicted flux = NANI (0.00035Q + 0.115), where Q is the average discharge. The predicted riverine N export is highly correlated (r^2 = 0.86, P = 1 × 10^{-10}) with the measured riverine N flux and is centered on the 1:1 line (WebFigure 8). For our large set of watersheds in Europe and the US, the multiyear average flux of N in rivers can be explained with a great deal of precision based simply on this NANI-discharge model.

Conclusions

The NANI approach provides a simple and robust method for estimating the flux of N from temperate-zone watersheds, including relatively small watersheds, as well as insight on the major sources of N pollution in the landscape. This evaluation of sources can provide guidance to water-quality managers regarding where to focus their efforts. For instance, field-scale agricultural practices should be the main focus for watersheds where N fertilizer dominates NANI, but treatment of wastes should be the greater focus for watersheds where the net import of N in food and feeds dominates. Although NANI alone is quite predictive for estimating riverine N flux, a model that includes both NANI and discharge increases the precision of the estimate. That the average flux of N in rivers increases as average multiyear discharge increases has profound implications for managing N pollution. Our finding suggests fewer long-term sinks for N in the landscape as it becomes wetter, with a greater percentage of NANI exported to coastal waters. Managers must consider this influence on N pollution in the face of a changing climate, where in the future some regions will become wetter and others drier.

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References

Aber J, Goodale C, Ollinger SV, *et al.* 2003. Is N deposition altering the N status of northeastern forests? *BioScience* **53**: 375–89.

Alexander RB, Johnes PJ, Boyer EW, and Smith RA. 2002. A comparison of models for estimating the riverine export of N from large watersheds. *Biogeochemistry* **57/58**: 295–339.

Bachman LJ, Krantz DE, and Bohlke J. 2002. Hydrogeologic framework, ground-water geochemistry, and assessment of N yield from base flow in two agricultural watersheds, Kent County, Maryland. Cincinnati, OH: US Environmental Protection Agency. EPA/600/R-02/008.

Billen G, Garnier J, Nemery J, *et al.* 2007. A long term view of nutrient transfers through the Seine River continuum. *Sci Total Environ* **275**: 80–97.

Billen G, Thieu V, Garnier J, and Silvestre M. 2009. Modelling the N cascade in regional watersheds: the case study of the Seine, Somme and Scheldt rivers. *Agr Ecosyst Environ* **133**: 234–46.

Boyer EW, Goodale CL, Jaworski NA, and Howarth RW. 2002. Anthropogenic N sources and relationships to riverine N export in the northeastern USA. *Biogeochemistry* **57/58**: 137–69.

Boyer EW, Howarth RW, Galloway J, *et al.* 2006. Riverine N export from the continents to the coasts. *Global Biogeochem Cy* **20**: GB1S91; doi:10.1029/2005GB002537.

Cleveland CC, Townsend AR, Schimel DS, *et al.* 1999. Global patterns of terrestrial biological N (N_2) fixation in natural systems. *Global Biogeochem Cy* **13**: 623–45.

David MB, Drinkwater LE, and McIsaac GF. 2010. Sources of nitrate yields in the Mississippi River basin. *J Environ Qual* **39**: 1657–67.

Donner SD and Scavia D. 2007. How climate controls the flux of N by the Mississippi River and the development of hypoxia in the Gulf of Mexico. *Limnol Oceanogr* **52**: 856–61.

EPA–SAB (US Environmental Protection Agency–Science Advisory Board). 2008. Hypoxia in the northern Gulf of Mexico: an update by the EPA Science Advisory Board. Washington, DC: US EPA. Report EPA-SAB-08-003.

Galloway JN, Dentener FJ, Capone DG, *et al.* 2004. N cycles: past, present, and future. *Biogeochemistry* **70**: 153–226.

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Han H and Allan JD. 2008. Estimation of N inputs to catchments: comparison of methods and consequences for riverine export prediction. *Biogeochemistry* **91**: 177–99.

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

Hirsch RM, Helsel DR, Cohn TA, and Gilroy EJ. 1993. Statistical analysis of hydrologic data. In: Maidment DR (Ed). Handbook of hydrology. New York, NY: McGraw-Hill.

Hong B, Swaney DP, and Howarth RW. 2011. A toolbox for calculating net anthropogenic nitrogen inputs (NANI). *Environ Modell Softw* **26**: 623–33.

Howarth RW, Billen G, Swaney D, *et al.* 1996. Riverine inputs of N to the North Atlantic Ocean: fluxes and human influences. *Biogeochemistry* **35**: 75–139.

Howarth RW, Ramakrishna K, Choi E, *et al.* 2005. Nutrient management, responses assessment. In: Ecosystems and human well-being, vol 3. Washington, DC: Island Press.

Howarth RW, Swaney DP, Boyer EW, *et al.* 2006. The influence of climate on average N export from large watersheds in the northeastern United States. *Biogeochemistry* **79**: 163–86.

Howarth RW, Chan F, Conley D, *et al.* 2011. Coupled biogeochemical cycles: eutrophication and hypoxia in coastal marine ecosystems. *Front Ecol Environ* **9**: 18–26.

Lewis WM. 2002. Yield of N from minimally disturbed watersheds of the United States. *Biogeochemistry* **57/58**: 375–85.

Lewis WM, Melack JM, McDowell WH, *et al.* 1999. N yields from undisturbed watersheds in the Americas. *Biogeochemistry* **46**: 149–62.

McDiffett WF, Beidler AW, Dominick TF, and McCrea KD. 1989. Nutrient concentration–stream discharge relationships during storm events in first-order streams. *Hydrobiologia* **179**: 97–102.

McIsaac GF, David MF, Gertner GZ, and Goolsby DA. 2001. Net anthropogenic N input to the Mississippi River basin and nitrate flux to the Gulf of Mexico. *Nature* **414**: 166–67.

NRC (National Research Council). 2000. Clean coastal waters: understanding and reducing the effects of nutrient pollution. Washington, DC: National Academies Press.

Peierls BL, Caraco NF, Pace ML, and Cole JJ. 1991. Human influence on river N. *Nature* **350**: 386–87.

Schaefer SC and Alber MA. 2007. Temperature controls a latitudinal gradient in the proportion of watershed N exported to coastal ecosystems. *Biogeochemistry* **85**: 333–46.

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

van Breemen N, Boyer EW, Goodale CL, *et al.* 2002. Where did all the N go? Fate of N inputs to large watersheds in the northeastern USA. *Biogeochemistry* **57/58**: 267–93.

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WebTable 1. International watershed data

Country/ region	Watershed	Area (km^2)	N export ($kg\ km^{-2}\ yr^{-1}$)	Temp (°C)	Precip ($mm\ yr^{-1}$)	Discharge ($mm\ yr^{-1}$)	NANI* ($kg\ km^{-2}\ yr^{-1}$)	Oxidized N deposition* ($kg\ km^{-2}\ yr^{-1}$)	Agricultural fertilizer ($kg\ km^{-2}\ yr^{-1}$)	Agricultural N fixation ($kg\ km^{-2}\ yr^{-1}$)	Net food/feeds ($kg\ km^{-2}\ yr^{-1}$)	"Natural" N fixation** ($kg\ km^{-2}\ yr^{-1}$)
NE US	Penobscot	20 109	320	4.3	1075	588	450	250	90	70	40	1122
NE US	Kennebec	13 994	330	4.3	1085	566	652	292	50	160	150	1197
NE US	Androscoggin	8451	400	4.6	1151	640	813	343	80	150	240	1179
NE US	Saco	3349	390	5.8	1218	672	640	400	40	100	100	1260
NE US	Merrimack	12 005	500	7.4	1148	589	1630	560	150	210	710	1291
NE US	Charles	475	1760	9.7	1207	583	3359	879	200	190	2090	1443
NE US	Blackstone	1115	1140	9.0	1260	651	2936	816	310	310	1500	1408
NE US	Connecticut	25 019	540	6.3	1160	642	1733	533	270	360	570	1195
NE US	Hudson	11 942	500	6.6	1126	622	1387	547	200	370	270	1162
NE US	Mohawk	8935	800	6.8	1142	548	2906	636	410	1240	620	1373
NE US	Delaware	17 560	960	8.7	1131	547	2372	812	530	680	350	1349
NE US	Schuylkill	4903	1760	10.6	1134	488	5321	931	1210	1230	1950	1494
NE US	Susquehanna	70 189	980	8.9	1022	487	3620	750	620	1150	1100	1235
NE US	Potomac	29 940	900	11.3	985	328	4359	719	1020	1170	1450	1520
NE US	Rappahannock	4134	470	12.6	1045	360	3791	711	1030	1440	610	1586
NE US	James	16 206	310	10.1	934	407	2107	647	360	700	400	1216
SE US	Roanoke	21 984	197	13.8	1181	352	2793	708	821	697	601	1923
SE US	Pamlico	5748	446	15.2	1155	334	4081	664	1892	848	803	1904
SE US	Neuse	7033	446	15.7	1200	341	4917	682	2262	824	1178	1993
SE US	Cape Fear	13 599	248	15.7	1186	355	3662	655	1061	530	1458	1927
SE US	Pee Dee	21 448	390	15.4	1220	467	4205	656	1181	1530	888	1745
SE US	Santee	32 017	312	15.6	1276	433	2630	671	556	496	909	1955
SE US	Black	3274	158	17.4	1213	286	3088	533	2010	839	–210	2152
SE US	Edisto	6944	228	17.9	1259	337	2839	546	1306	551	465	2140
SE US	Savannah	25 488	272	16.5	1339	418	2735	564	603	521	1053	2138
SE US	Ogeechee	8415	283	18.1	1260	330	2799	498	1594	730	5	2159
SE US	Altamaha	35 112	273	17.8	1252	339	3037	599	1138	572	750	2119
SE US	Satilla	7348	365	19.3	1299	275	3005	381	1678	137	817	2379
NW US	Deschutes	27 787	71	7.2	549	170	363	115	265	547	–563	870
NW US	Eel	8058	334	10.9	1205	704	283	184	59	199	–160	1155
NW US	Klamath	40 356	115	8.1	786	290	412	125	207	458	–378	1143
NW US	Merced	2876	99	10.5	697	110	868	227	338	164	153	1356
NW US	Nehalem	1747	1670	9.0	1862	1262	501	319	19	83	79	1387
NW US	Rogue	10 188	114	9.5	959	405	636	142	119	264	111	1279
NW US	Russian	3470	329	13.6	932	466	2440	258	388	513	1281	1073
NW US	Siuslaw	1531	1086	10.7	1584	1026	351	246	32	40	33	1289
NW US	Snake	279 438	93	6.0	537	136	472	94	652	633	–907	921
NW US	Spokane	9932	117	6.3	1135	516	338	171	165	83	–82	1431
NW US	Stanislaus	2485	106	10.0	822	205	1429	237	401	439	382	1427
NW US	Tuolumne	4307	80	9.8	704	133	1646	225	510	270	642	1319
NW US	Willamette	28 992	1065	9.6	1499	987	2677	268	1932	399	78	1181
NW US	Yakima	14 542	194	7.6	653	183	1836	149	1002	940	–255	1083
NW US	Santa Ana	3881	512	15.2	536	77	8522	870	658	1286	5711	1057
NW US	Pajaro	3063	460	14.0	406	34	2085	307	1019	1332	–573	853
NW US	Salinas	10 568	88	13.9	478	22	1833	228	2127	815	–1337	1050
Midwest US	Burns Ditch	857	1225	10.1	970	389	5440	814	6090	1924	–2695	1342
Midwest US	Escanaba	2253	216	5.0	846	326	529	355	35	104	39	1200
Midwest US	Ford	1165	211	5.2	810	313	1090	356	299	451	6	1146
Midwest US	Fox	15 825	381	7.1	801	259	4713	401	2000	2229	400	1251
Midwest US	Grand	14 292	777	8.6	838	296	4280	655	2754	1802	–509	1251
Midwest US	Kalamazoo	5164	579	8.8	899	365	3693	687	2449	1448	–467	1232

continued

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WebTable 1. International watershed data – *continued*

Country/ region	Watershed	Area (km^2)	N export ($kg\ km^{-2}\ yr^{-1}$)	Temp (°C)	Precip ($mm\ yr^{-1}$)	Discharge ($mm\ yr^{-1}$)	NANI* ($kg\ km^{-2}\ yr^{-1}$)	Oxidized N deposition* ($kg\ km^{-2}\ yr^{-1}$)	Agricultural fertilizer ($kg\ km^{-2}\ yr^{-1}$)	Agricultural N fixation ($kg\ km^{-2}\ yr^{-1}$)	Net food/feeds ($kg\ km^{-2}\ yr^{-1}$)	"Natural" N fixation** ($kg\ km^{-2}\ yr^{-1}$)
Midwest US	Manistee	4343	228	6.7	832	462	1297	515	291	524	–3	849
Midwest US	Manistique	883	290	5.7	834	456	497	369	38	110	–16	867
Midwest US	Menominee	10 541	206	5.0	780	291	815	328	153	340	16	1127
Midwest US	Milwaukee	1818	657	8.0	843	289	6731	588	2352	3108	1126	1279
Midwest US	Muskegon	6941	293	6.9	819	349	2336	552	663	1201	11	1083
Midwest US	Oconto	2543	369	6.1	798	279	2827	362	952	1337	329	1197
Midwest US	Peshtigo	2797	224	5.8	783	259	1549	346	460	641	164	1209
Midwest US	Pere Marquette	1764	298	7.3	909	360	1782	606	651	589	–1	1267
Midwest US	Root	510	1588	8.8	901	354	5942	764	2088	1825	1679	1263
Midwest US	Sheboygan	1106	811	8.1	856	235	8566	571	3801	3594	1107	1436
Midwest US	St Joseph	12 095	850	9.4	922	368	4356	698	3868	1903	–1473	1279
Midwest US	Trail Creek	153	832	10.0	969	510	4079	927	5265	2304	–3697	1057
France/Belgium	Armancon at Brianny	230	828	11.0	723	221	3955	450	4160	1028	–1682	1158
France/Belgium	Serre at Chaourse	251	1170	11.0	723	222	6158	450	9290	1202	–4784	1156
France/Belgium	Cousin at Avallon	350	729	11.0	723	384	3253	450	2112	872	–181	777
France/Belgium	Marne at Langres	368	1265	10.8	744	336	4059	550	5120	732	–2343	938
France/Belgium	Blaise at Wassy	389	3128	10.9	857	547	5118	550	8005	387	–3824	708
France/Belgium	Cure at Saint Père	563	689	11.2	702	473	2878	450	1486	1105	–163	519
France/Belgium	Rognon at Donjeux	629	2719	10.8	801	572	3340	550	4883	464	–2557	518
France/Belgium	Yonne at Dornecy	757	751	11.2	702	425	3984	450	2545	1402	–413	631
France/Belgium	Zenne at Eppegem	1137	3649	10.4	820	410	11 662	900	3068	287	7406	943
France/Belgium	Therain at outlet	1215	1686	10.4	674	293	6118	650	9132	916	–4581	873
France/Belgium	Aube at Bar-sur-Aube	1291	1549	10.8	678	432	2794	450	5000	435	–3091	558
France/Belgium	Saulx at outlet	2140	1799	10.3	897	436	5161	550	7850	460	–3699	1061
France/Belgium	Armançon at outlet	2983	2225	11.2	702	356	4892	450	7237	662	–3457	793
France/Belgium	Dijle at Haacht	3292	1546	10.4	820	278	6483	850	3044	278	2312	1252
France/Belgium	Somme at Abbeville	5566	1431	10.2	762	271	6058	530	12 346	1093	–7911	1131
France/Belgium	Scheldt at Asper	5959	2266	10.3	703	294	8605	650	8067	572	–684	940
France/Belgium	Eure at Lery	6002	1363	10.6	654	171	5923	550	11 072	897	–6596	1112
France/Belgium	Scheldt at Melle	10 015	2338	10.3	703	285	12 049	650	7918	594	2888	961
France/Belgium	Scheldt at Temse	12 306	2508	10.3	742	343	11 995	700	7172	589	3534	916
France/Belgium	Marne at Noisiel	12 832	1702	10.3	804	358	5667	550	8906	877	–4665	1026
France/Belgium	Oise at Creil	13 563	1840	10.2	682	353	5627	600	9507	1016	–5496	752
France/Belgium	Scheldt at Schelle	18 990	2390	10.3	742	346	11 058	800	5697	539	4023	908
France/Belgium	Scheldt at Doel	19 860	2311	10.3	742	327	11 217	800	5541	535	4341	953
France/Belgium	Seine at Alfortville	30 712	1692	10.8	697	277	5349	450	8750	781	–4632	966
France/Belgium	Seine at Poses	65 690	2004	10.6	716	310	5972	550	8756	841	–4175	933
UK	Afon Aeron	154	2260	8.7	1250	786	16 659	600	12 884	2907	268	1069
UK	River Bain	197	2500	9.5	668	188	10 841	800	16 157	1182	–7298	1106
UK	River Cam	141	1550	9.5	567	137	8432	1000	8800	558	–1926	989
UK	Esthwaite Water (lake)	16	1950	8.0	2387	1720	6360	1100	2972	1583	705	1544
UK	Fal Estuary	95	4404	11.0	1210	719	12 845	500	12 228	3264	–3147	1132
UK	Afon Glaslyn	69	1452	6.0	2790	2000	7018	1000	2205	1151	2662	1831
UK	Helford Estuary	115	4321	11.0	1210	779	12 382	500	10 764	3323	–2205	991
UK	Afon Irfon	244	1542	8.0	1840	1100	14 653	800	9315	2377	2161	1714
UK	River Lambourn	176	3575	9.3	736	258	3506	1000	11 522	878	–9894	1101
UK	River Leach	77	6760	9.4	735	376	7613	1000	16 055	1310	–10 752	823
UK	Lake Windermere	231	1410	8.0	2754	1900	6890	1100	2505	1403	1882	1981
UK	River Windrush	276	3732	9.4	763	389	9495	1000	13 245	1635	–6385	858
UK	Slapton Ley	46	5118	10.5	1035	550	14 424	800	12 679	3084	–2139	1118
UK	River Ryburn	51	1617	7.5	1260	340	12 571	1200	6233	3345	1793	2136
UK	River Crake	94	1894	7.2	1960	1420	20 041	1100	13 070	3431	2440	1246
UK	River Esk	72	1816	6.0	2260	1790	10 348	1200	5359	2680	1109	1083
UK	Midford Brook	147	7269	10.0	879	466	23 930	800	17 376	3413	2341	949
UK	River Meon	93	3333	9.4	920	339	12 191	1000	14 474	2011	–5294	1342
UK	River Erme	108	4124	9.8	1700	878	15 962	1100	12 105	3519	–762	1906

continued

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WebTable 1. International watershed data – *continued*

Country/ region	Watershed	Area (km^2)	N export (kg km^{-2} yr^{-1})	Temp (°C)	Precip (mm yr^{-1})	Discharge (mm yr^{-1})	NANI* (kg km^{-2} yr^{-1})	Oxidized N deposition* (kg km^{-2} yr^{-1})	Agricultural fertilizer (kg km^{-2} yr^{-1})	Agricultural N fixation (kg km^{-2} yr^{-1})	Net food/ feeds (kg km^{-2} yr^{-1})	"Natural" N fixation** (kg km^{-2} yr^{-1})
UK	River Cober	54	4815	11.0	1170	570	15 036	500	13 458	3611	–2533	1387
UK	Eastern Cleddau (estuary)	183	5332	9.5	1420	1030	15 229	500	10 135	3684	910	895
UK	River Ant	49	2061	10.0	631	156	8713	1000	15 764	1819	–9870	1094
UK	River Bure	402	2300	10.0	645	158	2375	1000	10 564	1375	–10 564	1122
UK	Deben Estuary	275	1900	10.2	593	143	8748	1000	16 147	1249	–9648	1036
UK	Ore/Alde Estuary	200	1810	10.2	592	148	4595	1000	14 136	3258	–13 799	1022
UK	River Kennet	1164	3479	9.4	774	294	16 418	1000	14 897	1605	–1084	1106
UK	Hampshire Avon	1706	3129	9.8	810	365	9127	1000	13 193	1133	–6199	1024
UK	Herefordshire Wye	4020	4728	9.3	1230	788	11 895	600	14 377	1690	–4772	1017
UK	Pilling Water	58	3812	9.4	1000	438	13 048	600	10 986	3814	–2352	1298
UK	Tamar Estuary	917	3930	10.2	1220	775	13 621	700	9144	3835	–58	1024
Sweden	Rickleån	1860	154	0.5	653	475	381	255	64	0	61	399
Sweden	Skellefte älv	11 577	128	–0.2	595	540	161	171	46	0	–56	110
Sweden	Pite älv	11 209	126	–0.2	595	341	178	162	22	0	–7	577
Sweden	Alterälven	476	167	0.1	624	692	534	215	298	0	20	–174
Sweden	Lule Älv	24 934	127	–0.2	540	593	184	139	68	0	–23	–141
Sweden	Kalix Älv	17 674	195	0.1	560	362	206	147	90	0	–30	446
Sweden	Torne älv	39 613	116	2.1	561	377	194	123	94	0	–23	415
Sweden	Forsmarksån	410	157	2.9	595	362	1123	347	410	0	366	528
Sweden	Dalälven	28 873	160	8.7	533	234	690	350	351	1	–11	682
Sweden	Gavleån	2279	195	7.6	836	651	400	388	306	1	–296	417
Sweden	Ljusnan	19 751	144	1.8	562	379	442	265	178	0	–1	410
Sweden	Delångersån	1975	108	4.3	612	287	465	287	132	1	45	744
Sweden	Ljungan	13 0422	110	5.9	552	175	378	224	172	0	–18	867
Sweden	Indalsälven	25 458	172	3.7	656	394	426	197	270	0	–42	596
Sweden	Ångermanälven	31 421	166	5.3	593	272	380	203	194	0	–18	732
Sweden	Ume älv	26 737	148	2.8	630	362	234	182	95	0	–43	610
Sweden	Råneälven	4137	97	5.7	641	231	234	182	62	0	–10	942
Sweden	Töreälven	406	182	5.6	622	380	239	206	51	0	–18	549
Sweden	Helge å	4684	549	7.0	656	193	3758	925	2127	6	700	1065
Sweden	Mörrumsån	3367	180	6.9	618	162	1163	867	427	0	–131	1050
Sweden	Lyckebyån	830	191	7.7	623	186	674	849	274	0	–449	1006
Sweden	Ljungbyån	689	299	7.8	602	171	1487	784	849	9	–154	991
Sweden	Emån	4559	100	8.4	590	136	1387	719	651	1	15	1045
Sweden	Botorpsströmmen	1040	99	6.8	790	293	1546	594	700	3	249	1147
Sweden	Motala ström	15 544	98	7.1	682	255	2697	591	1473	27	605	982
Sweden	Nyköpingsån	3258	150	7.4	586	241	2575	499	1507	19	551	791
Sweden	Norrström	22 534	108	7.4	586	192	2175	491	1590	17	76	904
Sweden	Rönne å	1896	475	6.2	595	208	5918	869	3674	56	1319	887
Sweden	Lagan	6353	290	6.2	595	220	1645	920	594	3	127	859
Sweden	Nissan	2738	398	5.6	622	257	975	933	359	2	–319	836
Sweden	Ätran	3364	426	1.3	574	475	2099	916	909	3	271	212
Sweden	Viskan	2153	610	1.3	574	468	1350	927	743	2	–321	231
Sweden	Göta Älv	48 214	260	6.8	790	204	1770	519	966	15	270	1354
Sweden	Gideälven	3322	148	5.2	602	221	281	256	28	0	–2	873
Sweden	Lögdeälven	1777	132	5.5	623	303	366	261	83	0	23	731
Sweden	Öreälven	2962	164	5.5	623	277	390	247	141	0	2	792

Notes: *NANI calculations for the US replace original estimates of atmospheric N deposition with estimates of oxidized N deposition from the USEPA CMAQ model for the same watershed areas. Other regions use oxidized N deposition based on the EMEP model. Notes: NANI components do not always sum to NANI because of rounding and other factors. NANI totals for SE and NW US watersheds include non-food export losses (Schaefer and Alber 2007; Schaefer *et al.* 2009). For midwestern watersheds, the NANI estimate most similar to the Howarth *et al.* (2006). calculation is reported (#7; Han and Allan 2008) adjusted for differences in N deposition estimates; steady-state, area-weighted values of the other NANI components are given as reported in Han and Allan (2008). For northwestern watersheds, 1992 data were used for those watersheds with sufficient information to estimate riverine N export (Schaefer *et al.* 2009) **Estimate of N fixation based on the evapotranspiration-based estimate of Cleveland *et al.* (1999) using the difference between watershed precipitation and discharge as an estimate of evapotranspiration Cleveland *et al.* 1999. Global patterns of terrestrial biological nitrogen (Nz) fixation in natural ecosystems. Global Biogeochem Cy 13: 623–45.

WebTable 2. Statistical output from multiple regression models to predict the riverine total nitrogen (TN) flux as a function of NANI, average discharge (Q), and average temperature (Temp) for the watersheds

*TN flux = b*NANI + c*NANI*Q + d*Temp (adjusted r^2 = 0.85)*

	NANI*Q	**NANI**	Temp
Coefficients	**0.00035**	**0.115**	–0.15
P value	**6×10^{-7}**	**8×10^{-6}**	0.98

*TN flux = b*NANI + c*NANI*Temp + d*Temp (adjusted r^2 = 0.81)*

	NANI	Temp	**NANI*Temp**
Coefficients	**0.364**	2.70	**–0.012**
P value	**6×10^{-7}**	0.75	**0.037**

*TN flux = b*NANI + c*NANI*Q (adjusted r^2 = 0.85)*

	NANI*Q	**NANI**
Coefficients	**0.00035**	**0.115**
P value	**5×10^{-10}**	**3×10^{-7}**

*TN flux = b*NANI + c*NANI*Q + d*Q (adjusted r^2 = 0.87)*

	NANI*Q	**NANI**	**Q**
Coefficients	**0.00031**	**0.1115**	**0.303**
P value	**3×10^{-8}**	**4×10^{-7}**	**0.022**

Notes: For the models shown here, the intercepts were set to zero. When intercepts were included in these models, they were never significant. Model parameters that are statistically significant are shown in bold. See Figure 2a in the main text for the simple model that relates TN flux to NANI alone. For the multivariate models that include temperature, the temperature terms are not statistically significant at the $P < 0.05$ level. On the other hand, for the models that include discharge, the terms involving discharge or the product of NANI and discharge are statistically significant at this level. This indicates that a model that includes discharge is more predictive than one that involves NANI alone (as in Figure 2a), while the inclusion of temperature gives no predictive power over a model based on NANI alone.

WebReferences

Cleveland CC, Townsend AR, Schimel DS, *et al.* 1999. Global patterns of terrestrial biological N (N_2) fixation in natural systems. *Global Biogeochem Cy* **13**: 623–45.

Han H and Allan JD. 2008. Estimation of N inputs to catchments: comparison of methods and consequences for riverine export prediction. *Biogeochemistry* **91**: 177–99.

Howarth RW, Swaney DP, Boyer EW, *et al.* 2006. The influence of climate on average N export from large watersheds in the northeastern United States. *Biogeochemistry* **79**: 163–86.

Johnes PJ. 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. *J Hydrol* **183**: 323–49.

Johnes PJ. 2007. Uncertainties in annual riverine phosphorus load estimation: impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. *J Hydrol* **332**: 241–58.

Johnes PJ, Moss B, and Phillips GL. 1996. The determination of water quality by land use, livestock numbers and population data – testing of a model for use in conservation and water quality management. *Freshwater Biol* **36**: 451–73.

Johnes PJ and Heathwaite AL. 1997. Modelling the impact of land use change on water quality in agricultural catchments. *Hydrol Process* **11**: 269–86.

Moss B, Johnes PJ, and Phillips GL. 1996. The monitoring and classification of standing waters in temperate regions – a discussion and proposal based on a worked scheme for British waters. *Biol Rev* **71**: 310–39.

Prior H and Johnes PJ. 2002. Regulation of surface water quality in a Chalk catchment, UK: an assessment of the relative importance of instream and wetland processes. *Sci Total Environ* **282/283**: 159–74.

Schaefer SC and Alber MA. 2007. Temperature controls a latitudinal gradient in the proportion of watershed N exported to coastal ecosystems. *Biogeochemistry* **85**: 333–46.

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

Uncles RJ, Fraser AI, Butterfield D, *et al.* 2002. The prediction of nutrients into estuaries and their subsequent behavior: application to the Tamar and comparison with the Tweed, UK. *Hydrobiologia* **475/476**: 239–50.

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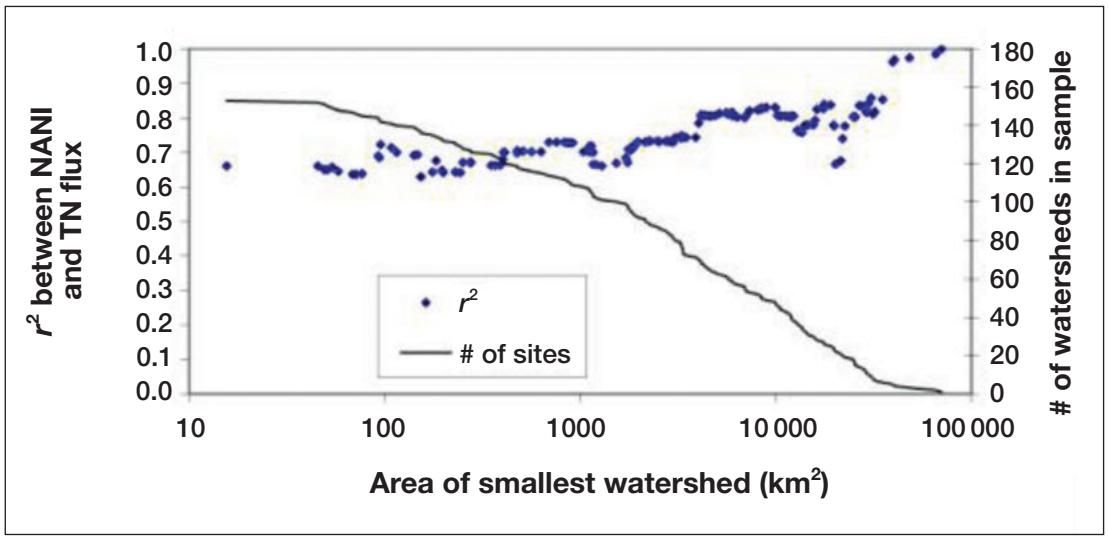
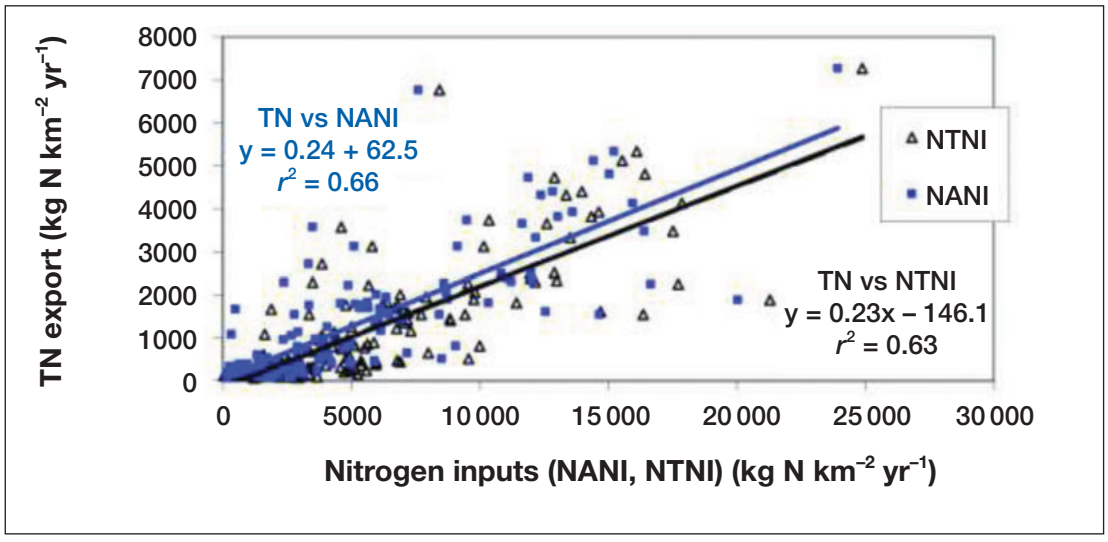


WebFigure 1. *Results of a step-wise analysis to determine the existence, if any, of a threshold influence on watershed size in the relationship between NANI and riverine nitrogen flux. We dropped one watershed at a time from the regression analysis between NANI and riverine nitrogen flux, always dropping the smallest remaining watershed, while recalculating the* r^2 *for the regression. In general, the* r^2 *increased as smaller watersheds were dropped, as we had predicted, but no sharp threshold was seen.*



WebFigure 2. *Comparison of net anthropogenic nitrogen inputs (NANI) and net total nitrogen inputs (NTNI) versus riverine nitrogen export for all 154 watersheds. NTNI includes an estimate for the natural rate of nitrogen fixation, whereas NANI does not. Both are highly correlated with riverine nitrogen flux, and the slopes of the relationships are significantly different from zero for both* ($P = 4 \times 10^{-37}$ *for NANI and* $P = 6 \times 10^{-35}$ *for NTNI). As discussed in the text, we estimate the natural rate of nitrogen fixation from a relationship between evapotranspiration and nitrogen fixation rates reported globally in Cleveland* et al. *(1999), given that data on the natural rate of nitrogen fixation are not available at the watershed scale for any of our watersheds. The estimate of the natural rate of nitrogen fixation is subject to large uncertainty, and a test of coincidence of the regressions shows no significant difference between the regression lines. For this reason, and because the use of NTNI provides no improvement in understanding riverine nitrogen fluxes over the use of NANI, we favor the use of NANI in this manuscript.*

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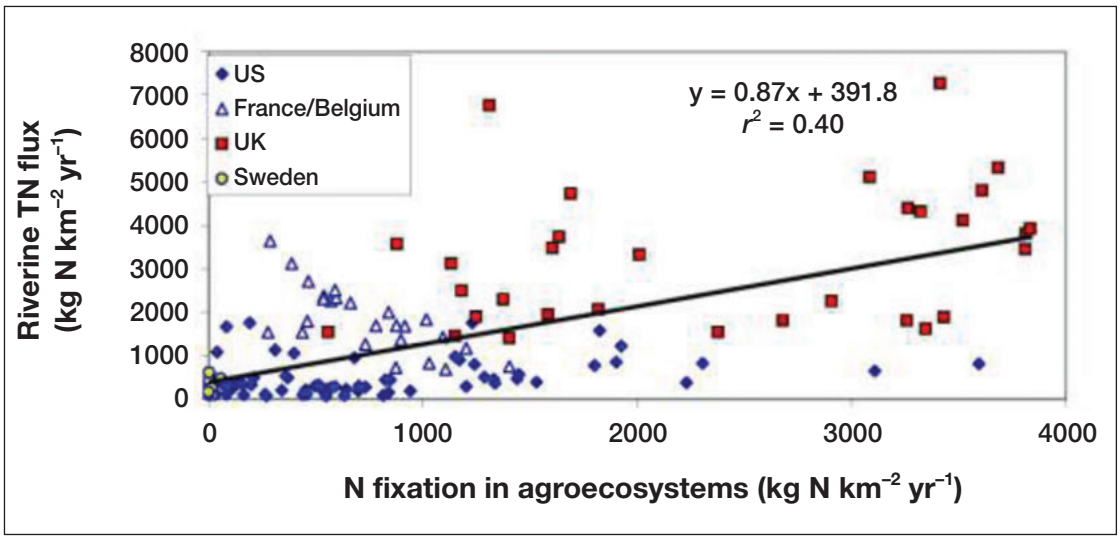
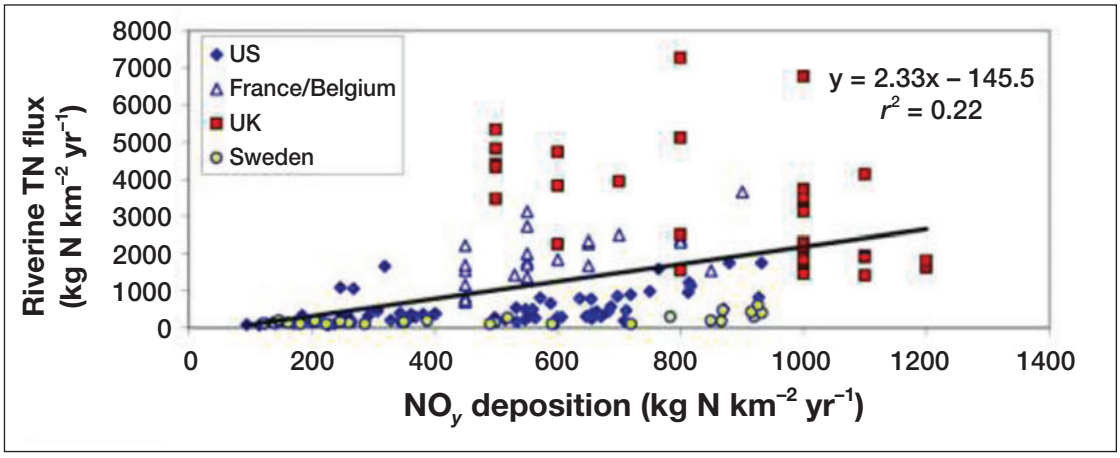


WebFigure 3. *The flux of nitrogen in rivers is correlated with the rate of nitrogen fixation associated with crops in agroecosystems across the 154 watersheds* ($P = 8 \times 10^{-19}$).



WebFigure 4. *The flux of nitrogen in rivers is correlated* ($P = 2 \times 10^{-9}$) *with the atmospheric deposition of oxidized nitrogen* (NO_y) *across the 154 watersheds. Much of the scatter in this figure is the result of very large inputs of nitrogen from other sources, such as fertilizer and net inputs in food and feed, which ultimately contribute to the magnitude of the riverine TN flux. The relationship between* NO_y *deposition and riverine nitrogen flux for those watersheds where the nitrogen input in deposition equals or exceeds the input from synthetic fertilizer is much stronger (see Figure 3b in the main text).*

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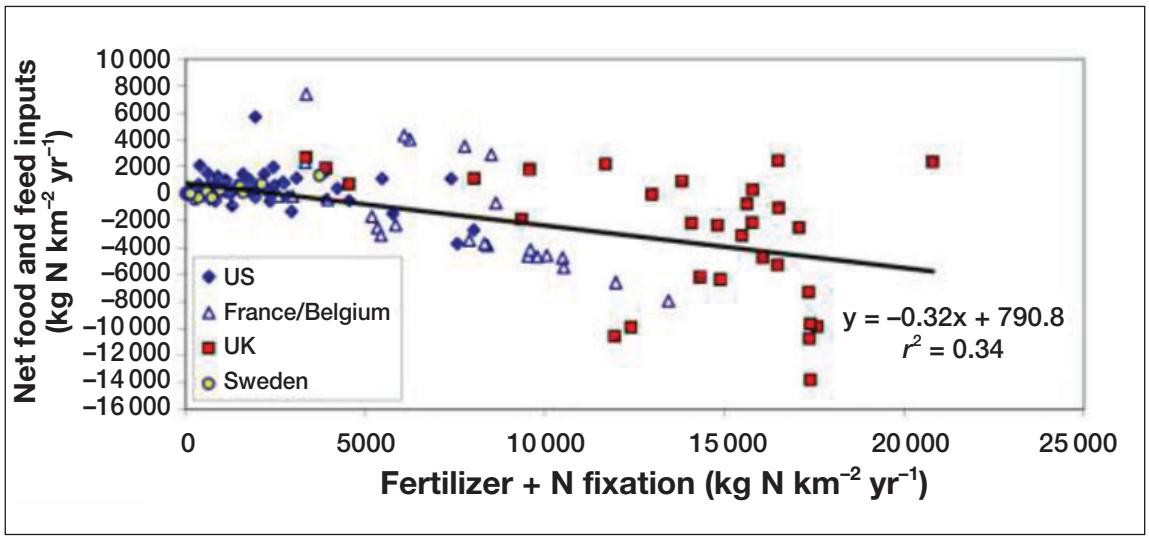

WebFigure 5. *The input of nitrogen to the landscape as synthetic fertilizer and as nitrogen fixation associated with agroecosystem is well correlated* ($P = 2 \times 10^{-15}$) *with the net inputs of nitrogen in food and feed to the landscape across the 154 watersheds. This explains in part why the riverine nitrogen flux from watersheds that have a large net negative input of nitrogen in food and feeds (ie a large export of food) is so high: the riverine fluxes are driven by the input of synthetic nitrogen fertilizer, which also supports the high export of food and feeds (see Figure 4 in the main text).*

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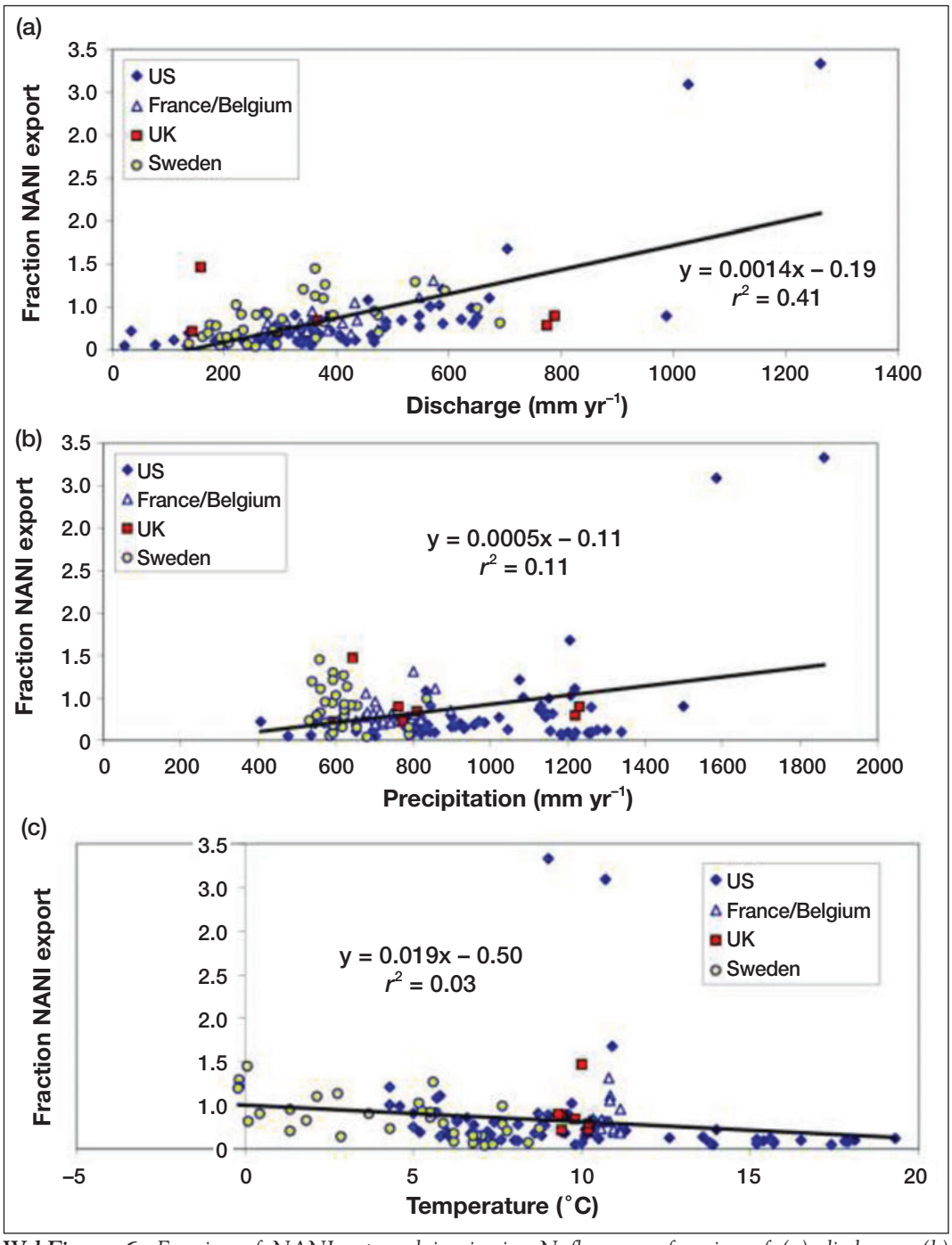

WebFigure 6. *Fraction of NANI exported in riverine N flux as a function of (a) discharge, (b) precipitation, and (c) temperature for all watersheds greater than 250 km^2. The fraction of NANI that is exported in rivers is well correlated with the discharge in individual watersheds (P = 5 x 10^{-16}). Precipitation and temperature also show weaker but significant relationships (P = 9 x 10^{-5} , P = 3.7 x 10^{-2}, respectively), and with far less explanatory power (r^2 values of 0.41, 0.11, and 0.03 for discharge, precipitation, and temperature, respectively). For most watersheds, between 0% and 100% of NANI (fractions of 0.0 to 1.0) is exported, with greater export when discharge is higher. The two watersheds with the greatest discharge also show very high fractional export of NANI (> 3.0), which is not possible in a sustained way over time without some other nitrogen input. These watersheds are in Oregon on the west coast of the US, and are known to have very high rates of natural nitrogen fixation in alder swamps and in other forest soils, which is not included in NANI and may explain the high riverine nitrogen export. Note that the relationship of Cleveland* et al. *(1999) that we used to estimate nitrogen fixation for NTNI in WebFigure 2 highly underestimates the reported rate of natural nitrogen fixation in these watersheds.*

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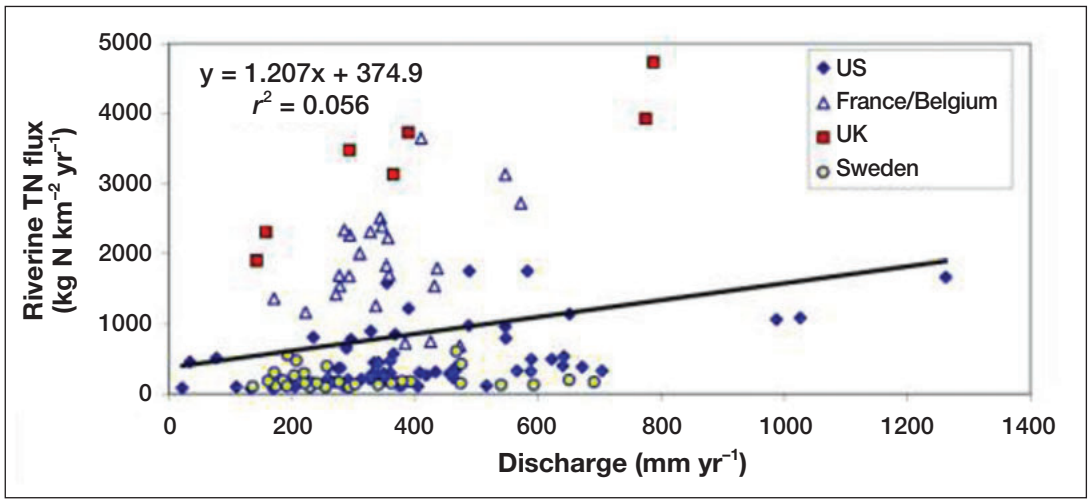
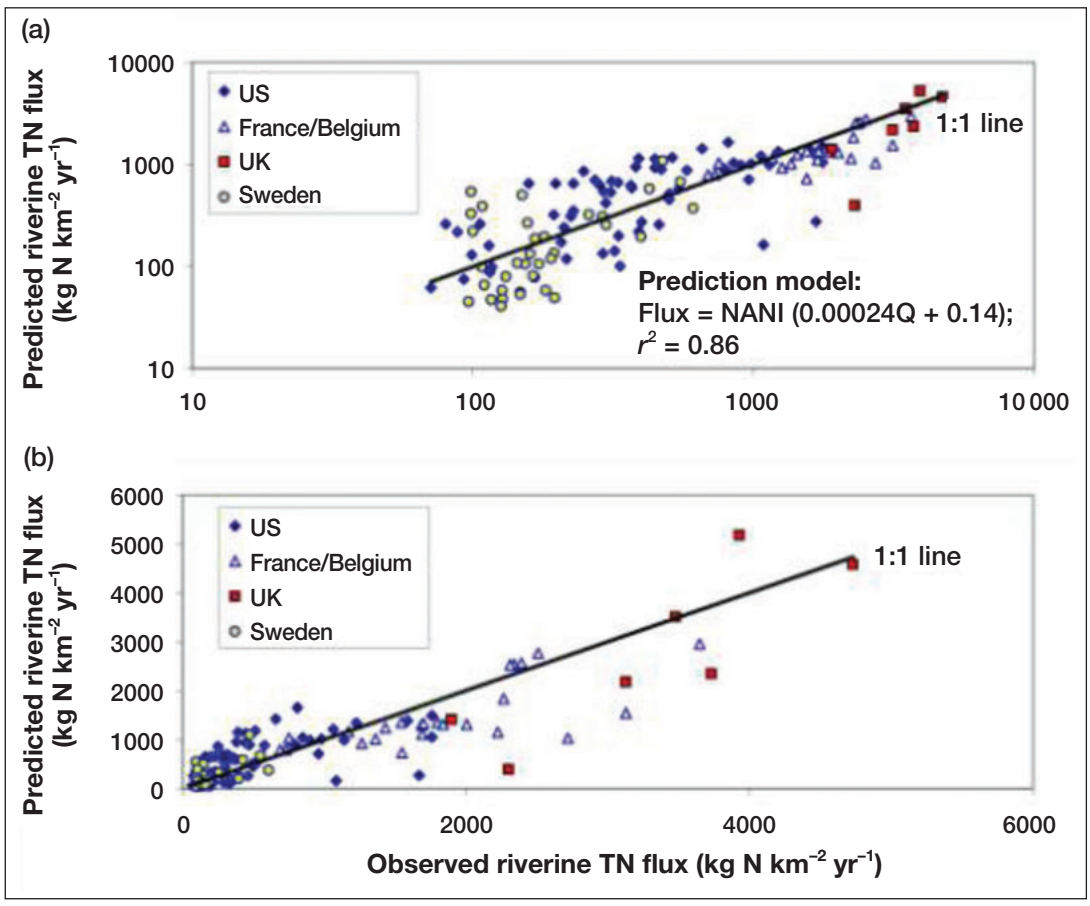


WebFigure 7. *The TN flux of nitrogen in rivers is correlated (P = 0.007) with the discharge across watersheds for watersheds greater than 250 km^2, but discharge explains only a small proportion of the variability of the flux, and so the usual concern about autocorrelation between riverine flux and discharge seems unfounded for this analysis. Much of the scatter in the figure is the result of the spatial distribution of inputs of nitrogen, as captured by NANI (see Figure 2 and WebFigure 2).*



WebFigure 8. *Predicted versus observed riverine nitrogen flux for all watersheds greater than 250 km^2. The observed riverine nitrogen flux (x-axes) is well correlated with the riverine nitrogen flux estimated from a simple model of flux = NANI (0.00024q + 0.14) (y-axes) for both (a) log–log scale and (b) linear scales. The P value of the zero-intercept, bivariate regression is 1 x 10^{-10}.*