Report

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# Human Impact on Nitrate Export: An Analysis Using Major World Rivers

We developed a simple model that related $NO_3$ export to point-source N loading and nonpoint source N loads from chemical fertilizers and $NO_y$ deposition and tested it at the global scale using data from 35 large rivers with a global distribution. The model explained well ($r^2 > 0.8$) the nearly 1000-fold variation in $NO_3$ export from different regions of the world. The model suggests that human activity is the dominant control of $NO_3$ export even though less than 20 of the 100 Tg N $yr^{-1}$ added to land in fertilizer and $NO_y$ deposition is at present exported from rivers as $NO_3$. Watershed export to rivers may increase in the future due to either increased loads to the watershed or decreased watershed retention. Simple models, coupled with continued measurements of $NO_3$ in rivers, will be of use in interpreting these regional changes.

## INTRODUCTION

In many estuaries, and in coastal seawater, concentrations of available N limit primary production (1, 2). Thus, factors that increase N loading can have serious or critical impacts on the functioning of coastal ecosystems (3, 4). One important way in which N is loaded to the coast is in river flow (5). These rivers obtain their N from diffuse inputs from the watersheds (nonpoint sources) and by inputs directly to the river (point sources) (6). Humans have increased N loading to terrestrial systems through a variety of processes including the manufacture of fertilizer and the use of high temperature internal combustion engines (7). The nature of the linkage between increased human loading of N to watersheds and the output of that N to coastal waters is not straightforward. The export of N applied to terrestrial systems depends on a myriad of factors including hydrology, geology (slope, soil type), and human alteration of landscape by forest clearing and wetland destruction (8). Given this complexity, it is not surprising that there have been few attempts to study the variation and controls of N loading to coastal waters at the regional to global scale (but see 9–11). Rather, much of the research has been focused on process-level studies at more manageable scales (12–15). Nitrogen pollution, however, is a regional to global-scale problem and we need to understand the linkage between N input and N output at the appropriate scale.

The study of rivers offers an opportunity to examine the effects of anthropogenic loading on export as chemical constituents in these rivers serve as integrative measures of land-water exchange at the watershed scale (16–19). Further, for very large rivers, the watershed encompasses entire regions, and regional export can then be compared to regional anthropogenic loading. These comparisons allow insights into both which human activities are important to export across regions, and estimates of regional-scale retention (20).

In this paper, we attempt to determine the importance of various human activities which influence N export at the regional to global scale using data from the world's major watersheds. In particular, we focus on the impacts of humans on increased N loading to terrestrial systems through fertilizer application and $NO_y$ deposition, and the impact of point sources (sewage) added directly to rivers. Prior studies on large rivers with global distribution have shown that both $NO_3$ and $PO_4$ export are related to human population density in the watershed ($r^2 \sim 0.5$) (9, 20). Additionally, for $PO_4$, a simple model that included point source and nonpoint inputs gave a better prediction of river export than did human population alone, and allowed evaluation of the importance of various human activities in controlling P export in different regions of the world (20). Further, this model gives insights into the magnitude and controls of watershed retention at the regional scale. In this study, we use a similar approach considering $NO_3$ export.

## APPROACH

Our data set includes 35 large river systems with worldwide distribution (Table 1). For each of these systems, there are relatively good estimates of average annual $NO_3$ export. We can compare these export values to those predicted from a simple loading model:

$$\text{modeled } NO_{3\,export} = (R_{export})^x [\text{Point Inputs} + (WS_{export})^x (\text{WS Inputs})]. \qquad \text{Eq.1}$$

where $R_{export}$ and $WS_{export}$ are the export coefficients (the fraction of loaded N that is exported) from rivers and watersheds, respectively. Point Inputs and WS Inputs are the amounts of N that is loaded to the river and watershed, respectively. These loading terms and the N export by rivers are expressed as average loading over the area of the watershed (kg N $km^{-2}$ $yr^{-1}$). For point

**Table 1. Characteristics of 35 rivers used in N export model. Runoff is water runoff in meters per year. Urban population is in humans per km² of watershed and fertilizer load, $NO_y$ input and River Export are all in kg of N per km² of watershed per year.**

| | Runoff | Urban Population | Fertilizer Load | NOy Input | River Export |
|---|---|---|---|---|---|
| Adige | 0.58 | 68 | 2889 | 1093 | 541 |
| Amazon | 0.78 | 1 | 14 | 150 | 33 |
| Columbia | 0.37 | 7 | 323 | 100 | 62 |
| Danube | 0.25 | 47 | 3546 | 729 | 153 |
| Delaware | 0.60 | 74 | 1320 | 752 | 518 |
| Ganges | 0.47 | 78 | 1521 | 250 | 198 |
| Glama | 0.53 | 9 | 656 | 400 | 179 |
| Huanghe | 0.14 | 42 | 809 | 253 | 276 |
| Hudson | 0.51 | 111 | 1100 | 752 | 356 |
| Kazan and Back | 0.19 | 0 | 3 | 100 | 3 |
| Mackenzie | 0.19 | 0 | 8 | 100 | 12 |
| Magdalena | 0.99 | 20 | 192 | 200 | 235 |
| Mekong | 0.60 | 6 | 617 | 250 | 144 |
| Meuse | 0.29 | 240 | 8132 | 655 | 920 |
| Mississippi | 0.16 | 22 | 1530 | 611 | 177 |
| Murray-Darling | 0.01 | 1 | 29 | 90 | 1 |
| Niger | 0.20 | 4 | 24 | 250 | 21 |
| Nile | 0.01 | 22 | 1470 | 45 | 3 |
| Orange | 0.01 | 11 | 374 | 100 | 4 |
| Orinoco | 1.07 | 2 | 64 | 150 | 96 |
| Parana | 0.18 | 7 | 36 | 200 | 50 |
| Po | 0.70 | 155 | 2820 | 1093 | 681 |
| Rhine | 0.37 | 258 | 7128 | 1455 | 1520 |
| Rhone | 0.56 | 73 | 4095 | 615 | 491 |
| St. Lawrence | 0.33 | 11 | 162 | 600 | 65 |
| Susquehanna | 0.48 | 74 | 1342 | 726 | 437 |
| Thames | 0.12 | 368 | 3808 | 993 | 1120 |
| Tiber | 0.43 | 176 | 3485 | 1093 | 587 |
| Uruguay | 0.33 | 8 | 56 | 200 | 135 |
| Vistula | 0.17 | 73 | 3913 | 736 | 165 |
| Volga | 0.19 | 33 | 1190 | 134 | 80 |
| Ysngtze | 0.37 | 42 | 1209 | 328 | 495 |
| Yukon | 0.23 | 0 | 34 | 50 | 32 |
| Zaire | 0.33 | 4 | 27 | 150 | 30 |
| Zambezi | 0.08 | 5 | 333 | 250 | 10 |

inputs we consider human sewage, for watershed inputs we consider fertilizer application and atmospheric deposition.

Total human sewage production was calculated by a per capita N contribution of 1.85 kg $person^{-1}$ $yr^{-1}$ which is the low end estimate of Vollenweider (21). This N contribution is consistent with the relatively high N consumption in Europe and North America coupled to a removal of N during sewage treatment of about 60% and lower N consumption in Asia and Africa coupled with a removal during sewage treatment (21–23). To get total human point source inputs, we multiplied the per capita input by an estimate of population in each watershed that is sewered. This estimate was base on urban population estimates (20, 24), as urban population sewage generally goes directly to large river systems, while for rural populations it does not (20, 23).

An estimate of loading of fertilizer to the watershed of each river was calculated as the product of N fertilizer use per unit of agricultural land and the area of agricultural land in the watershed (20, 25). Atmospheric deposition of $NO_y$ inputs were reported from direct measurements for each watershed (9) or modeled deposition of $NO_y$ (26). Where direct estimates were wet deposition, we multiplied values by 2 to get wet and dry inputs (27).

Not all of the N loaded to watersheds reaches coastal waters. N retention (due to storage and loss of gaseous N) can occur in both watersheds and in rivers (8, 28). For river systems a large number of variables that could influence within-river retention could be mentioned. One of the few studies that has, however, attempted to quantify within-river retention is that of Billen et al. (29). Their work suggests that river retention, due to denitrification and net burial, is generally near 30% of N loading. We use this value for all our systems ($R_{export} = 0.7$). The systems studied by Billen et al. did not have impoundments. The potential influence of impoundments will be discussed later.

We use two simple models to calculate the watershed export coefficient ($WS_{export}$):

Model 1. constant values across all systems; and

Model 2. values that vary with hydrologic output

Such that:

$$WS_{export} = C \times WL^{X} \qquad \text{Eq. 2}$$

Where: WL is the average water output from the watershed in m $yr^{-1}$, C and X are constants.

To determine which watershed retention model works best (1 or 2), and to determine the best formulation of each model, we use a best-fit approach. That is, our criteria for choosing a retention model is that it results in the best fit between actual measurements of $NO_3$ export and those predicted from our simple model (Eq. 1).

## N SOURCES AND EXPORT

### Point Loading to the River

For our 35 river systems the calculated point source input from human sewage varied by over 3 orders of magnitude from 0.2 to 672 kg $km^{-2}$ $yr^{-1}$ (expressed on a watershed areal basis to make comparison to watershed loading terms). The Thames had the highest calculated point-source input. This high value reflects both the high population densities in this watershed (400 individuals $km^{-2}$) and the high degree of urbanization (92%). The MacKenzie River, with extremely low population density in the watershed, had the lowest calculated sewage loading.

On average, for the 35 river systems, the point-source loading is 107 kg $km^{-2}$ $yr^{-1}$, and is, thus, 20-fold less than the average watershed loading from precipitation and fertilizer. This point source loading is not, however, subject to retention in the watershed or riparian areas. Thus, where N retention is high, the point-source loading may become far more important than these numbers suggest. Interestingly, some studies that have compared the importance of point-source inputs to watershed loadings (8, 30), have neglected to consider the watershed retention of the nonpoint input.

### N Loading to the Watershed

We considered loading of N to the watershed from atmospheric deposition and fertilizer application. Atmospheric deposition inputs varied from 50 to 2700 kg $km^{-2}$ $yr^{-1}$ in different systems and averaged 743 kg $km^{-2}$ $yr^{-1}$. Fertilizer inputs varied between 2 and 8132 kg $km^{-2}$ $yr^{-1}$, and averaged at 1550 kg. The sum of these inputs varied between 84 and 9830 in the different watersheds, with a mean value of 2293 kg $km^{-2}$ $yr^{-1}$. The Rhine had the highest calculated watershed loading, and in this system fertilizer loading and atmospheric deposition accounted for 73% and 27% of the inputs to the watershed, respectively. The high input by fertilizer reflects both the high input of N per unit agricultural land in this watershed and the high proportion of agricultural land. Three arctic watersheds, the Kazan and Back, the MacKenzie and the Yukon have the lowest estimated N loadings to the watershed (near 100 kg $km^{-2}$ $yr^{-1}$). In these systems, precipitation dominated loading estimates to the watershed.

### Watershed Runoff Coefficients

The simplest possible model of watershed export is the use of constant export coefficients across all watersheds. The use of constant values of retention between 0.05 and 0.45 showed similar explanatory power between measured and modeled $NO_3$ export ($r^2 = 0.59$ to 0.61). A value of 0.15 gave the best fit in terms of closeness of fit (1:1 relationship between measured and modeled values).

We also modeled N export from watersheds as a function of water yield. When this was done we were able to achieve a much better fit between measured and modeled export, and the parameters that best fit were with C = 0.4 and X = 0.8 (Eq. 2). With these parameters we predict that, at the world average runoff of 0.3 m $yr^{-1}$, 15% of the N loaded as precipitation and fertilizer leaves as $NO_3$ runoff; at runoffs of 0.1 and 1 m $yr^{-1}$, we estimate 6.3 and 40% runoff, respectively. These runoff coefficients are in the range of those found in the literature (8).

The variable hydrologic model predicted well measured $NO_3$ export from watersheds. We show this by comparing measured and modeled values in terms of range of values, mean values and overall fit. For measured export, the lowest value was in the Murray-Darling where an estimated 1.5 kg N $km^{-2}$ $yr^{-1}$ leaves the watershed. The highest values were in the Rhine where 1590 kg N $km^{-2}$ $yr^{-1}$ leaves the watershed as $NO_3$ in rivers. The modeled export from the watersheds has a very similar range (2.5 and 1520 kg N $km^{-2}$ $yr^{-1}$, respectively), and places the same river systems at the extremes (Fig. 1). For the 35 systems, the average measured and modeled values were 368 and 294 kg $km^{-2}$ $yr^{-1}$, respectively. Linear regression analysis demonstrates that measured and calculated $NO_3$ export are closely related. Both log-log and linear regression of modeled *versus* estimated $NO_3$ export give highly significant relationships ($r^2$ = 0.80 and 0.89, respectively; both $p < 0.001$) (Fig. 2). In addition, these relationships show close to 1:1 correspondence between modeled and measured values (Figs 1 and 2).

Of the 35 river systems examined, 26 of the systems show extremely close agreement between measured and modeled export; the ratio of modeled to measured export in these systems varied between 0.5 and 2.0. There were, however, 3 systems where modeled estimates exceeded measured export by 3-fold or more. A common feature of these 3 systems (the Zambezi, the Orange, and the Nile River) is that they have large reservoirs in the main channels with long residence times. Perhaps these reservoirs are responsible for decreasing the $NO_3$ export by decreasing $R_{export}$, a parameter we fixed at 0.7.

### Predicted Importance of Loading Terms

We model $NO_3$ export as resulting from precipitation, fertilizer, and point-source inputs. Not surprisingly, the importance of these various modeled inputs varied considerably between different systems (Fig. 1, bottom panel). The relative importance of fertilizer inputs tended to increase with increasing population in the watershed ($p = 0.02$), while the relative importance of precipitation and point inputs were related significantly to both population and water runoff. Precipitation inputs were positively related to runoff and negatively related to population while point sources had opposite relationships to these 2 variables. Thus, $NO_3$ export in the Thames (with very high population and moderate runoff) as well as the Orange (with very low runoff and moderately low population) is dominated by point-source inputs in our model. For the 35 river systems, fertilizer inputs are on average the most important N source to rivers (roughly 50% of inputs). Precipitation and point sources showed similar importance (ca. 25%). This distribution of N sources is in agreement with some regional level studies of N inputs (31, 32).

## DISCUSSION

The export of N from large rivers varies dramatically from region to region (11). There is growing evidence that most of this variation is related to human activity in the watershed. Cole et al. (9) showed that human population alone explained over 50% of the 1000-fold variation in $NO_3$ export in world rivers. Jordan and Weller (33) demonstrated that the 100-fold regional variation in $NO_3$ export in the continental United States related well to anthropogenic N loads to the watershed. Similarly, Howarth et al. (10) demonstrated that the roughly 20-fold variation in total N export from sub-regions adjoining the North Atlantic was related well to total anthropogenic N load to the watershed. Our results, using a global data set, suggest that $NO_3$ export is related to human-induced N load to the watershed and direct point loads of $NO_3$ to rivers and a simple model that includes only these inputs explains over 80% of the variation in $NO_3$ export between systems.

In the studies of Cole et al. (9), Jordan and Weller (33), and our study, only $NO_3$ export was considered. Nitrogen is transported in rivers, however, in several forms including nitrate, ammonium, and dissolved organic N (DON) and in some systems $NO_3$ may account for less than 10% of the total N export by the river (11). The fact, then, that $NO_3$ export alone is related to human population or activity in the watershed suggests either that $NO_3$ (and not other forms of N) is extremely sensitive to human-induced watershed changes, or that $NO_3$ represents a constant (and perhaps small) proportion of the human impact on N across systems. That is, $NO_3$ export is not the total of human impacts on N export, but is an indicator of this impact. River data on $NO_3$ and total dissolved N (TDN) show that the answer is a combination of these 2 possibilities. That is, a linear regression of $NO_3$ and other forms of TDN *versus* population in the watershed show that both $NO_3$ and other forms of dissolved N increased with increasing population. The $NO_3$ has, however, both a stronger relationship to population and increases more sharply with population than do other forms of TDN (Fig. 3). This higher slope suggests that changes in $NO_3$ account for much of the total human impact on N export.

In our study, and other recent studies, watershed loads of N were shown to relate relatively closely to river export of N or $NO_3$. This close relationship may seem surprising as watershed retention of N is potentially extremely variable across regions as it is influenced by a great number of variables including: geology (slope and rock type), vegetation type, and watershed disturbance (8); retention is also influenced by a variety of factors including oxygen content of waters and sediment type (27, 34). Further, we did not consider all new N inputs (7, 10), the most significant of which are natural inputs of N from nitrogen fixation (35). One might expect, therefore, that a model that ignored

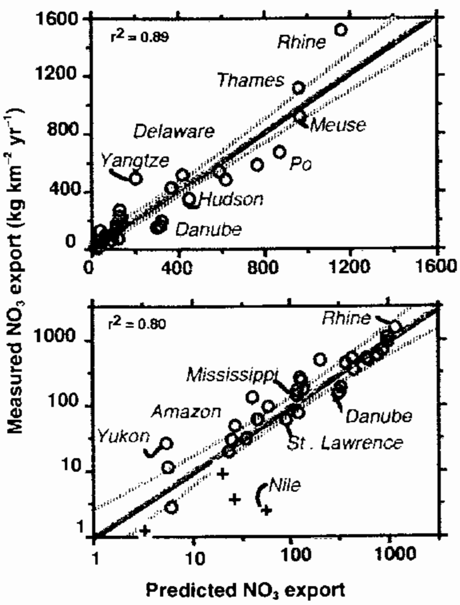


Figure 1. Measured *versus* modeled $NO_3$ export from 35 river basins with a global distribution. The relationship is shown both as a linear plot (top panel) and a log-log plot (bottom panel). For both panels the solid red line is the regression line and the stippled red lines are the 95% confidence intervals around that line. Each blue circle or cross represents a river system (only some are labeled). The systems with crosses shown in the log-log plot (lower panel) represent dry systems (runoff < 0.1 m yr$^{-1}$). Both linear and log-log regressions of measured *versus* modeled export are highly significant ($p < 0.001$) and have slopes (1.02 and 0.99) and intercepts (7.5 and 0.003) not significantly different from 1 and 0, respectively. $NO_3$ data are from Meybeck (11), Peierls et al. (19) and Caraco (20).

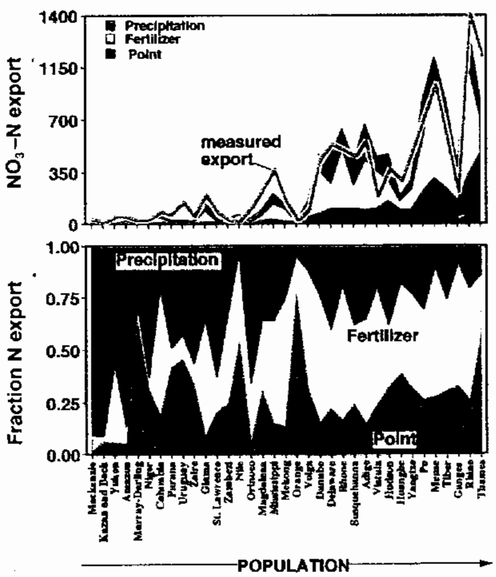


Figure 2. (Top panel) $NO_3$ export (kg N m$^{-2}$ yr$^{-1}$) as measured (red line) in river water and as independently modeled from the sum of precipitation, fertilizer, and point (sewage) inputs in 35 river basins with global distribution. (Bottom panel) The 3 modeled inputs as a percent of total input for the same rivers. In both panels, the river basins are arranged in order of increasing human population density in the watershed.

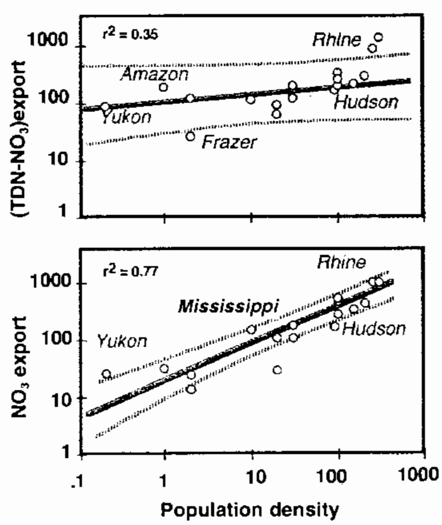


Figure 3. Population density in the watershed *versus* $NO_3$ export (bottom panel) and other forms of dissolved N (TDN-$NO_3$, top panel) for 16 rivers, primarily in Europe and North America. For both forms of N, export is in kg N m$^{-2}$ yr$^{-1}$. For both panels, the solid red line is the regression line and the stippled red lines are the 95% confidence intervals around that line. Each blue circle represents a different river system (only some are labeled). $NO_3$ and TDN data are from Meybeck (11).

all of these variables, would not predict well the N export from aquatic systems. So why does our model, which considers only the influence of hydrology on retention, and ignores natural N loads, work? We believe that natural inputs could be ignored in our model of $NO_3$ as these inputs are related to organic N export while human inputs of N in fertilizers and $NO_y$ deposition are related more to $NO_3$ export (Fig. 3). Possibilities that explain why retention could be modeled include:

*i)* Many of the factors shown to be important in controlling retention of N at the plot or small watershed scale are not important in controlling retention at the regional scale.

*ii)* Many of the factors that control retention are constant across regions. For example, the presence of intact wetlands could be important in controlling N retention, but if relatively nonvariable across large regions, could be rolled into a simple retention coefficient and not explicitly treated.

*iii)* There is an inverse correlation between controls of retention. For example, if dam construction (which could increase retention) was inversely related to wetland destruction (which would decrease retention), then a model ignoring both these terms might still have good predictive power.

Although the underlying factors for variable (or constant) N retention across systems are not fully understood, we know that at present retention of N on the regional scale is large. This means that at present the impact of humans on N export is not as great as it might be, given the potential for lower N retention in the future.

On a global scale, roughly 100 Tg N $yr^{-1}$ is loaded to land from fertilizer and N derived by fixation in internal combustion engines. Because much of this N is loaded to areas with 0.2–0.4 m $yr^{-1}$ water runoff (23, 35), about 15% of this N or 15 Tg is exported to rivers. In the future N loading to watersheds from fertilizer and precipitation inputs will likely increase (36, 37). Further, the prospects of global-scale changes in N retention can not be ignored. Presently, the majority of N loaded to watersheds in fertilizer and precipitation is not lost by runoff. A large fraction of this loaded N is either stored in soils and biota or lost to denitrification (38, 39). A critical question is: will the retention of human-produced N remain high?

Studies at the small watershed to plot scale suggest that the capacity to retain N can ultimately saturate as N loadings to systems increase (40, 41). To date there have been few studies of N saturation and decreased N retention at the regional scale. If this decrease in N retention occurs, it would contribute greatly to increased N loading from terrestrial to aquatic systems. The continued study of large rivers may allow us to detect these changes. The construction of simple output models will help elucidate the roles that retention and loading play in causing changes in regional N losses.

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