Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico

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An increase in the flux of nitrogen from the Mississippi River during the latter half of the twentieth century has caused eutrophication and chronic seasonal hypoxia in the shallow waters of the Louisiana shelf in the northern Gulf of Mexico[1-5]. This has led to reductions in species diversity, mortality of benthic communities, and stress in fishery resources[4]. There is evidence for a predominantly anthropogenic origin of the increased nitrogen flux[2,5-7], but the location of the most significant sources in the Mississippi basin responsible for the delivery of nitrogen to the Gulf of Mexico have not been clearly identified, because the parameters influencing nitrogen-loss rates in rivers are not well known. Here, we present an analysis of data from 374 US monitoring stations, including 123 along the six largest tributaries to the Mississippi, that shows a rapid decline in the average first-order rate of nitrogen loss with channel size—from 0.45 day^{-1} in small streams to 0.005 day^{-1} in the Mississippi River. Using stream depth as an explanatory variable, our estimates of nitrogen-loss rates agreed with values from earlier studies. We conclude that the proximity of sources to large streams and rivers is an important determinant of nitrogen delivery to the estuary in the Mississippi basin, and possibly also in other large river basins.

The problem of tracing nitrogen through large watersheds stems from the difficulty of establishing a spatially continuous mass balance between three rate variables: the in-stream flux of nitrogen, the rate of nitrogen supply from atmospheric and terrestrial sources, and the rate of removal due to denitrification and storage on the landscape and in stream channels. Much of the controlled study of supply and removal processes has taken place in relatively small watersheds[6] where landscape and channel conditions are less variable. Few measurements of nitrogen loss rates are available for the relatively heterogeneous basins typical of large river channels. Moreover, the reported range of nitrogen loss rates for stream and river channels exceeds two orders of magnitude, and few explanations for this large variability have emerged. Although various physical and chemical properties of rivers[6,8-13] are known to influence nitrogen loss rates, including oxygen concentrations, the organic content of benthic sediments, channel depth, water travel time (that is, water residence time), and streamflow, little has been reported about how loss rates vary over a range of river sizes. In the absence of systematic knowledge of nitrogen loss rates in channels, no accepted method has emerged for predicting nitrogen transport over long channel distances. Thus, recent efforts[7,14] to identify the location and types of sources in the Mississippi River basin responsible for nitrogen entering coastal waters have met with only limited success.

We used a recently developed mass-balance method[12] (SPARROW—SPAtially-Referenced Regression On Watershed attributes) to estimate nitrogen flux through the interior watersheds of the Mississippi basin, refining the technique to more precisely quantify nitrogen transport in large channels such as those in the Mississippi River and its major tributaries. The regression model and the compilation of the spatial watershed data on nitrogen source inputs, physical characteristics of the landscape, and attributes of the digital stream network have been previously described[12] (see Supplementary Information). The method correlates observations of stream nitrogen flux (that is, the response variable) with spatially referenced explanatory data on nitrogen source inputs (for example, fertilizer use, atmospheric deposition) and factors controlling nitrogen transport in watersheds, including physical characteristics of the landscape (for example, soil permeability) and aquatic systems (for example, channel size, water velocity). The structural

form of the model, which contains separate landscape and stream parameters, provides empirical estimates of the rates of terrestrial and in-stream removal of nitrogen (see table 1). The response variable in the spatial regression model is mean stream nitrogen flux computed from water-column measurements of total nitrogen (TN; sum of nitrate-nitrite and kjeldahl nitrogen—ammonia plus organic nitrogen) in filtered samples and daily flow measurements[15] at 374 river locations in the United States. These monitoring locations include a subset of 123 stations in the watersheds of six major tributaries to the Mississippi River (Fig.1). The mean flux estimates at all stations are adjusted to reflect 1987 nitrogen inputs and long-term mean flow conditions, based on the records of concentration and flow for the period 1978 to 1992. Source inputs for 1987 are representative of average inputs over at least the past two decades (see Supplementary Information).

The regression results show that the mean first-order rate of total nitrogen loss (fraction of nitrogen removed per unit water travel time) is inversely related to channel size, and spans nearly two orders of magnitude (Table 1) over the range of rivers studied. To reliably estimate the functional form over the wide range of river sizes, channel size is defined according to four discrete streamflow classes. Benthic denitrification, a biologically-mediated process, is expected to be the prominent loss process quantified by the empirical in-stream loss rates, but the long-term physical storage and release of particulate nitrogen on flood plains and in reservoirs[16,17] may also be reflected by the rate coefficients. The inverse relation between in-stream nitrogen loss and channel size is probably explained by the influence of channel depth (that is, water stage) on particulate nitrogen settling times and the supply of nitrate for denitrification[10,18]. The supply of nitrate to benthic sediments is controlled by the direct diffusion of nitrate nitrogen in the water column[6,8,10,18], the nitrification of ammonia supplied by mineralized organic nitrogen[8,19], and the exchange of nitrogen-enriched stream water in the hyporheic zone[20-22]. Channel depth is a measure of the volume of stream water available for processing by a unit area of benthic sediment. Thus, nitrogen removal via denitrification and settling generally decreases in deeper channels where less contact and exchange of stream waters occurs with the benthic sediment. A previous study[6] described the percentage aquatic nitrate loss as a declining function of the ratio of depth to water travel time, but did not express nitrogen loss as a rate, and thus did not separate the effect of depth from travel time.

We plotted the empirically derived SPARROW loss rates vs. mean stream depth in Fig. 2 based on an empirical transformation of stream flow. We compared these estimates of in-stream loss with the available literature estimates[6,8,11,13,23-28] for the larger temperate watersheds for which estimates of water travel time could be obtained. The travel time of water in streams governs the time of exposure of stream nitrogen to removal processes, including the settling of organic particulate nitrogen, exchange of ground and surface waters (i.e., hyporheic flow)[20-22], and nitrate diffusion to the benthic sediment[8,18,19]. Few empirical studies of in-stream nitrogen removal are available, and even fewer studies report estimates for total nitrogen and large rivers as analysed in this study. The available literature estimates of percentage nitrogen removal were re-expressed as a loss rate per unit water travel time and plotted as a function of depth. The transformed rates agree reasonably well with the magnitude and declining monotonic pattern of the SPARROW rates of in-stream loss over a wide range of channel depths (Fig. 2). Similar agreement was also found for in-stream loss rates plotted as a function of stream flow. These findings provide limited confirmation of the validity of the SPARROW rates of nitrogen loss. Moreover, the findings demonstrate the consistency of the literature loss estimates over a considerable range of river sizes when nitrogen loss is expressed as a rate (per unit water travel time) and plotted as a function of depth. In Fig. 2, the greatest agreement in loss rates appears in the larger rivers deeper than one metre, where the literature rates show the least variability and are within a factor of two of the SPARROW rates. For depths above four metres, relatively close agreement is found in the rates of nitrogen loss in the freshwater tidal reaches of the Potomac and Delaware[8] (0.003 and 0.006 per day, respectively) and the SPARROW rate of 0.005 per day. In rivers with mean depths less than one metre, greater variability generally exists among the literature and SPARROW rates. This may be explained by the greater influence of benthic processes (and variations in benthic conditions, such as the organic content and degree of oxidation of sediments) on nitrogen loss in shallow streams.

Figure 2 indicates that the first-order rate of nitrogen removal in streams (that is, *k* in Table 1) declines rapidly with increasing channel size as in-stream loss processes become progressively less effective with increases in channel depth. At the basin scale, depth and water velocity increase (as water travel time per

unit channel length decreases) in a downstream direction[29]. Each of these changes in stream attributes contributes to a decrease in stream nitrogen loss per unit channel length. In the Mississippi basin, the decrease in nitrogen loss per unit length due to increases in depth is approximately three times greater than the decrease in loss per unit length due to increases in velocity (see Supplementary Information). To assess the total effect of changes in the first-order loss rate and water velocity on nitrogen delivery to the Gulf of Mexico from interior river locations in the Mississippi basin, we applied the rate coefficients in Table 1 to river network data on channel size and water travel time. We quantified the percentage of the nitrogen export from each of the outlets of 742 interior watersheds in the Mississippi basin that is delivered by streams to the Gulf (Fig. 3; see Supplementary Information for the absolute quantities of nitrogen delivered by source). On the basis of this analysis, we find that the region of high nitrogen delivery to the Gulf is dendritic in shape and extends far upstream along the major tributaries in the eastern and central portions of the basin (for example, Ohio, Tennessee, Lower Missouri, Lower Arkansas and Upper Mississippi rivers). Despite the long water travel times, many watersheds located on large rivers more than 2,500 kilometres from the Gulf deliver significantly larger fractions of their exported nitrogen (some more than 90%) to coastal waters than watersheds located on smaller streams less than a few hundred kilometres from the Gulf. In addition, the dendritic pattern of nitrogen transport leads to widely varying delivery percentages in each of the major regional drainages of the Mississippi basin, ranging from more than 90% from watersheds on the largest rivers to substantially less than 40% from watersheds on small streams (see Table 3 in Supplementary Information). This wide variation is evident despite similarities of the distances of interior watersheds from the Gulf of Mexico within each regional drainage. Nitrogen deliveries from many arid watersheds in the more distant drainages of the western Mississippi basin (that is, the western portions of the Missouri and Arkansas/Red regions) are uniformly small because of the effect of the typically shallow rivers with high nitrogen-loss rates and the lengthy water travel times to the Gulf.

We conclude that, because the nitrogen loss rate in streams declines rapidly with increasing channel size, knowledge of the length of time that surface waters are transported through channels of varying size can help to predict the quantities of nitrogen delivered from interior locations to coastal waters. Despite uncertainty in the rate of nitrogen loss in stream channels of a given size, the evidence of a large, systematic decline in the rate of nitrogen removal from small streams to large rivers has important implications for nutrient management in the Mississippi river basin, and more generally, in large coastal watersheds. The delivery of nitrogen to coastal systems from point and diffuse sources is not a simple function of the distance of these sources from coastal waters. Instead, the proximity of sources to large streams and rivers, as measured by the length of time that surface waters travel through smaller tributaries, is a major determinant of their downstream transport to marine systems. Information on the rates of nitrogen delivery to coastal waters may assist in evaluations of efficient nutrient control strategies, including efforts to identify the most significant watersheds and sources contributing to riverine exports of nitrogen to coastal ecosystems.

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1. Rabalais, N. N., *et al.*, Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf, *Estuaries* 19, 386-407 (1996).
2. Turner, R. E. and N. N. Rabalais, Coastal eutrophication near the Mississippi river delta. *Nature* **368**, 619-621 (1994).
3. Vitousek, P.M., *et al.*, Human alteration of the global nitrogen cycle: sources and consequences, *Ecol. Appl.* **7**, 737-750 (1997).
4. Diaz, R.J. & R. Rosenberg, Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna, *Oceanog. Mar. Biol. (Annu. Rev.)* **33**, 245-303 (1995).
5. Turner, R.E. & N.N. Rabalais, Changes in Mississippi River water quality this century: implications for coastal food webs, *BioScience* **41**, 140-147 (1991).
6. Howarth, R.W., *et al.*, Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences, *Biogeochemistry* **35**, 75-139 (1996).
7. Goolsby, D.A., *et al.*, Flux and sources of nutrients in the Mississippi-Atchafalaya River basin (Report of Task Group 3 to the White House Committee on Environment and Natural Resources, Hypoxia Work Group) *Federal Register* **64**, 23834-23835 (1999).
8. Seitzinger, S.P., Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance, *Limnol. Oceanogr.* **33**, 702-724 (1988).

9. Seitzinger, S.P. & C. Kroeze, Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems, *Glob. Biogeochem. Cycles* **12**, 93-113 (1998).
10. Kelly, C.A., *et al.*, Prediction of biological acid neutralization in acid-sensitive lakes, *Biogeochemistry* **3**, 129-141 (1987).
11. Behrendt, H., Inventories of point and diffuse sources and estimated nutrient loads—a comparison for different river basins in central Europe, *Wat. Sci. Tech.* **33**, 99-107 (1996).
12. Smith, R.A., G.E. Schwarz & R.B. Alexander, Regional interpretation of water-quality monitoring data, *Wat. Resour. Res.* **33**, 2781-2798 (1997).
13. Preston, S.D. & J.W. Brakebill, *Application of Spatially Referenced Regression Modeling for the Evaluation of Total Nitrogen Loading in the Chesapeake Bay Watershed* (U.S. Geological Survey Water Resources Investigations Report 99-4054, Baltimore, Maryland, 1999).
14. Brezonik, P.L. *et al.*, Effects of reducing nutrient loads to surface waters within the Mississippi River Basin and the Gulf of Mexico (Report of Task Group 4 to the White House Committee on Environment and Natural Resources, Hypoxia Work Group) *Federal Register* **64**, 23834-23835 (1999).
15. Alexander, R.B., Slack, J.R., Ludtke, A.S., Fitzgerald, K.K. & T.L. Schertz, Data from selected U.S. Geological Survey national stream water quality monitoring networks, *Wat. Resour. Res.* **34**, 2401-2405 (1998).
16. Johnston, C.A., G.D. Bubenzer, G.B. Lee, F.W. Madison & J.R. McHenry, Nutrient trapping by sediment deposition in a seasonally flooded lakeside wetland, *J.Environ. Qual.* **13**, 283-290 (1984).
17. Billen, G., S. Dessery, C. Lancelot & M. Meybeck, Seasonal and inter-annual variations of nitrogen diagenesis in the sediments of a recently impounded basin, *Biogeochemistry.* **8**, 73-100 (1989).
18. Baker, L.A. & P.L. Brezonik, Dynamic model of internal alkalinity generation: calibration and application to precipitation-dominated lakes, *Wat. Resour. Res.* **24**, 65-74 (1988).
19. Novotny, V., and H. Olem, *Water Quality: Prevention, Identification, and Management of Diffuse Pollution* (Van Nostrand Reinhold, New York, 1994).
20. McMahon, P.B., & J.K. Bohlke, Denitrification and mixing in a stream-aquifer system: effects on nitrate loading to surface water, *J. Hydrol.*, **186**, 105-128 (1996).
21. Triska, F.J., Duff, J.H., & R.J. Avanzino, Patterns of hydrological exchange and nutrient transformation in the hyporheic zone of a gravel-bottom stream: examining terrestrial-aquatic linkages, *Freshwat. Biol.*, **29**, 259-274 (1993).
22. Harvey, J.W., Wagner, B.J., & K.E. Bencala, Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange, *Water Resour. Res.*, **32**, 2441-2451 (1996).
23. Hill, A., Denitrification in the nitrogen budget of a river ecosystem, *Nature* **281**, 291-292 (1979).
24. Hill, A., Nitrate-nitrogen flux and utilization in a stream ecosystem during low summer flows, *Can. Geogr.* **XXV**, 225-239 (1981)
25. Sjodin, A.L., Lewis, W.M., Jr. & J.F. Saunders, III, Denitrification as a component of the nitrogen budget for a large plains river, *Biogeochemistry* **39**, 327-342 (1997).
26. Burns, D.A., Retention of NO3 in an upland stream environment: a mass balance approach, *Biogeochemistry* **40**, 73-96 (1998).
27. Billen, G., Lancelog, C. & M. Meybeck, *N, P, and Si Retention Along Aquatic Continuum from Land to Ocean, In Ocean Margin Processes in Global Change*, (eds. Mantoura, R.F.C., Martin, J.M. & Wollast R.) 19-44 (Wiley, 1991).
28. Twidwell, S.R. & J.R. Davis, *Intensive Surveys of San Antonio River Segments 1901 and 1911, June 6, 1984 – May 16, 1985* (Texas Natural Resource Conservation Commission, IS 87-04, Austin, Texas, 1987).
29. Leopold, L.B. & T. Maddock, Jr., *The Hydraulic Geometry of Stream Channels and Some Physiographic Implications* (U.S. Geological Survey Professional Paper 252, Reston, Virginia, 1953).
30. Seaber, P.R., Kapinos, F.P. & G.L. Knapp, *Hydrologic units maps* (U.S. Geological Survey Water Supply Paper, 2294, Reston, Virginia, 1987).

Supplementary information is available on *Nature's* World-Wide Web site (http://www.nature.com) or as paper copy from the London editorial office of *Nature*.

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Table 1 SPARROW spatial regression model coefficients for total nitrogen

Model Parameters	Coefficient Units	Bootstrap Coefficient	Lower 90% CI	Upper 90% CI
Nitrogen source, β				
Point sources	dimensionless	0.394	0.094	0.639
Fertilizer application	dimensionless	1.37	0.605	2.34
Livestock waste production	dimensionless	0.903	0.012	1.97
Atmospheric deposition	dimensionless	4.78	1.84	8.21
Nonagricultural land	kg ha^{-1} yr^{-1}	18.6	6.18	29.3
Land-to-water loss coefficient, α				
Temperature	$^{o}F^{-1}$	0.017	0.009	0.023
Soil permeability	hr. cm^{-1}	0.036	0.024	0.049
Drainage area per stream length	km^{-1}	0.043	0.017	0.063
In-stream loss rate coefficient, *k*				
k_1 ($Q < 28.3$ m^3 s^{-1})	day^{-1}	0.455	0.344	0.579
k_2 (28.3 m^3 $s^{-1} < Q < 283$ m^3 s^{-1})	day^{-1}	0.118	0.063	0.176
k_3 (283 m^3 $s^{-1} < Q < 850$ m^3 s^{-1})	day^{-1}	0.051	0.007	0.092
k_4 ($Q > 850$ m^3 s^{-1})	day^{-1}	0.005	0.000	0.019

Coefficients are estimated in a spatial non-linear least-squares regression of stream nitrogen flux at 374 monitoring locations on watershed characteristics, based on a robust bootstrap estimation procedure[12] (r-squared=0.881; MSE=0.435; see Supplementary Information for explanation of the SPARROW model and coefficients). The nonpoint-source coefficients (β) multiplied by an exponential land-to-water delivery function (i.e., $e^{-\alpha z}$, where z is a vector of land-to-water loss factors; for example, temperature) quantify the proportion of available nitrogen mass delivered to rivers as a function of the specified source inputs and landscape characteristics. The land-to-water delivery function is equal to one for point-source inputs. The rate coefficients (*k*) quantify the first-order rate of in-stream nitrogen loss per unit of water travel time (for example, k_4=0.5% removal of nitrogen per day of water travel time). The regression residuals provide acceptable adherence to model assumptions. In-stream loss rates are fit separately for stream reaches with mean stream flow (Q) corresponding to the indicated intervals. Nitrogen loss rates (for example, k_4) were estimated according to a continuous function of streamflow in preliminary analyses; however, a discrete functional form defined by separate stream flow classes provides the most accurate fit to the observational data for the extreme river sizes; the uppermost class has great significance to large rivers in the Mississippi basin. Model predictions of flux are typically within 32% of the observed values based on the median of station values (interquartile range from 15 – 61%). A validation of the model predictions through comparisons with an independent data set of 68 monitoring stations in the Chesapeake Bay watershed in the eastern United States provided reasonable confirmation that the predictions are relatively unbiased (model predictions are typically within 39% of the observed values with an interquartile range from 19 – 82%), and that the residuals accurately describe the unexplained variability in the model from which confidence intervals (CI) are developed.

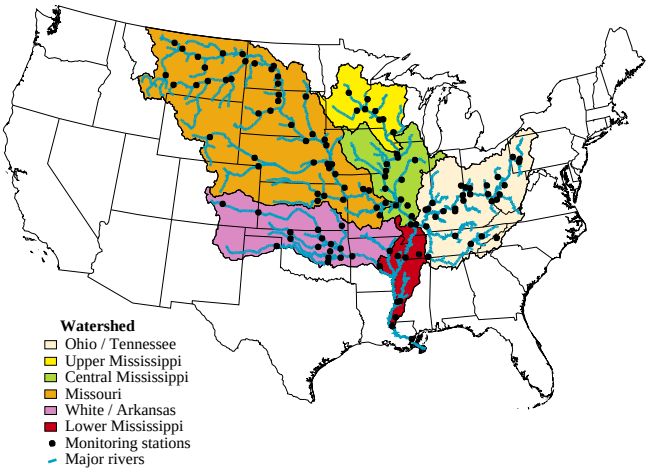

Figure 1 River monitoring stations and major regional watersheds in the Mississippi river basin.

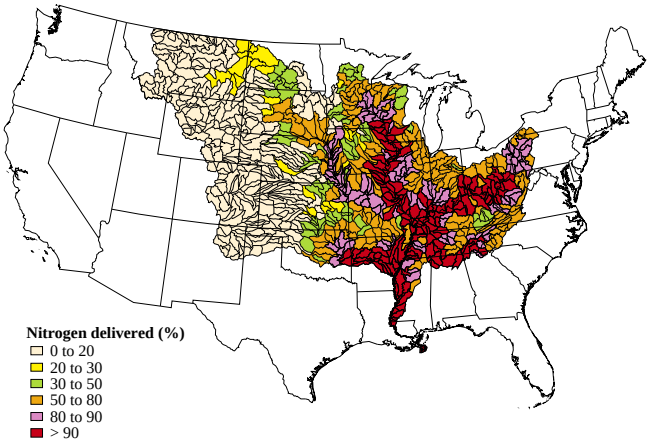

Figure 3 Percentage of the nitrogen export from interior watersheds delivered to the Gulf. Approximately equally sized interior watersheds, ranging from about 2,400 to 4,900 km^2 (mean is 3,900 km^2), are systematically defined according to the hydrologic cataloging unit classification[30]. The delivery percentage is the fraction of the nitrogen exported from inland watersheds that remains after in-stream transport to the Gulf, and is computed as [exp(-$k't$)100], where k' is a vector of SPARROW estimates of in-stream nitrogen loss for four stream sizes (Table 1), and t is a vector of mean water travel times from each watershed outlet to the Gulf for each of the four stream sizes. The water travel times from locations above the diversion from the Lower Mississippi river to the Atchafalaya river are computed as the flow-weighted mean of the travel time (2.4 days) for each pathway to the Gulf. See the Supplementary Information for regional estimates of the delivery percentages and the absolute quantities of nitrogen delivered by source.

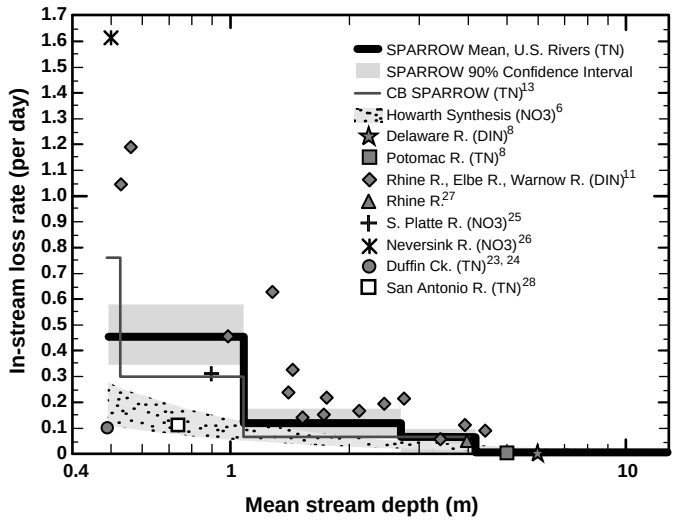

Figure 2 Nitrogen-loss rate in relation to stream channel depth. Stream flow is empirically transformed by regressing observations of mean depth on mean stream flow, on the basis of data from a study of stream morphology and hydraulics at 112 river locations in the United States[29] (stream depth and flow are monotonically related according to $D = 0.2612S^{-0.3966}$, where D is mean stream depth in metres and S is mean stream flow in m^3s^{-1}; R^2=0.83). Literature estimates of in-stream nitrogen loss, L (expressed as a fraction of external inputs), are re-expressed as a loss rate (per unit water travel time), R, according to $R = -t^{-1} \ln(1 - L)$, where t is the water time of travel and ln is the natural logarithm. Loss rates are reported for the following nitrogen forms: total nitrogen (TN), nitrate-nitrogen (NO_3), and dissolved inorganic nitrogen (DIN). SPARROW refers to the mean nitrogen-loss rates estimated in this analysis. CB SPARROW refers to mean estimates separately derived for streams of the Chesapeake Bay watershed over depths of 0.5 to 4 m (ref. 13). Water travel times were estimated for the Rhine, Elbe and Warnow[11] rivers from river network data[12] for watersheds in the northeastern quadrant of the United States, based on a regression of the mean water travel time, T, from headwater reaches to the outlet reach of each watershed in units of days on total drainage area, A, in units of square kilometres (R^2=0.88, T=-0.0065 + $0.2642A^{0.3}$). The mean time of travel for watershed streams is computed as one half of T. These estimates assume similar hydraulic properties and drainage density for the European and US watersheds. Channel depths for data from the Rhine river[27] and the European watersheds[11] were determined from the empirical transformation of stream flow given above. The graphed range of loss rates for nitrate, based on a synthesis of denitrification measurements from selected watersheds in North America[6], is computed as the ratio of mass transfer coefficients (representing the height of the water column from which nitrate is removed per unit time) to mean depth.