Coastal and Estuarine Studies

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Nitrogen Loading in Coastal Water Bodies *An Atmospheric Perspective*

American Geophysical Union Washington, D.C.

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Atmospheric Nitrogen Flux From the Watersheds of Major Estuaries of the United States: An Application of the SPARROW Watershed Model

Richard B. Alexander, Richard A. Smith, Gregory E. Schwarz, Stephen D. Preston, John W. Brakebill, Raghavan Srinivasan, and Percy A. Pacheco

Abstract

To assess the atmospheric contributions of total nitrogen (TN) in riverine exports to coastal and estuarine ecosystems in the United States, we applied a nationally calibrated empirical watershed model, SPARROW (Spatially Referenced Regression on Watershed attributes), to a selected set of 40 major coastal watersheds. In contrast to conventional statistical watershed models, SPARROW uses a mechanistic structure in the correlation of observations of stream nitrogen load with spatial data on contaminant sources, landscape characteristics, and stream properties, allowing separate estimation of the quantities of nitrogen delivered to streams and the outlets of watersheds from point and diffuse sources. We calibrated the model using data from a national set of 374 watersheds. Application of the model to the 40 coastal watersheds indicates that atmospheric nitrogen contributions to riverine export range over nearly two orders of magnitude, from 4 to 326 kg km⁻² yr⁻¹. The atmosphere is estimated to contribute from 4 to 35 percent of the TN in stream export with a median of 20 percent. The highest atmospheric contributions are observed in the northeastern and Mid-Atlantic watersheds of the United States. Uncertainties in the estimates, based on the standard error of prediction, range from 40 to 100 percent and vary inversely with watershed size. Agricultural sources typically contribute the largest share of nitrogen (more than one third in most basins), followed by the aggregate contributions of other diffuse sources.

Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective Coastal and Estuarine Studies, Pages 119-170 Copyright 2001 by the American Geophysical Union Municipal and industrial point sources are similar in magnitude to atmospheric contributions in most watersheds, but represent the largest share (35-88%) of nitrogen in one half of the North Atlantic watersheds and in several watersheds of the Gulf region. Comparisons of the SPARROW model with other national and regional watershed models indicate general agreement in the predictions of TN export over a wide range of watershed sizes. Assessments of atmospheric sources to coastal watersheds are likely to benefit from a continued effort to integrate the mechanistic descriptions of deterministic models with the empirical methods of estimating watershed-scale rate processes and their uncertainties in statistical models.

1. Introduction

An increase in the flux of nitrogen to coastal marine systems during the latter half of the 20^{th} century has caused eutrophication of many temperate estuaries, including numerous estuarine systems in the United States such as the Chesapeake Bay, Louisiana shelf, and New York bight [Diaz and Rosenberg, 1995; Vitousek et al. 1997]. Although there is ample evidence that the problem is predominantly cultural in origin [Nixon, 1995; Vitousek et al. 1997], uncertainties remain over the relative importance of the various human activities that supply nitrogen to coastal waters. Use of nitrogenous fertilizers, atmospheric emissions of nitrogenous compounds, and point-source discharges of nitrogenous wastes have all increased significantly since 1950 [CEQ, 1989; NASS, 1998; Alexander and Smith, 1990; Battaglin and Goolsby, 1994]. To date, information on the relative importance of the major anthropogenic sources of nitrogen in coastal systems has been frequently obtained by comparing the quantities of nitrogen released to the environment from those sources (e.g., Howarth, et al., 1996]. Due to denitrification, storage, and biological utilization of nitrogen in the watershed, however, only a fraction of the released nitrogen is ultimately transported to coastal waters. Moreover, the fraction transported from each local source is a function of both sourcedependent and source-independent (e.g., stream channel properties) characteristics of the watershed, and has been difficult to reliably estimate [Alexander et al. 2000]. Nevertheless, such information is needed for efficient management of coastal ecosystems because the cost effectiveness of controlling individual nitrogen sources varies with the fraction of the nitrogen from each source that is transported to coastal waters.

Assessing the r^)le of atmospheric sources of nitrogen in coastal eutrophication is an important example of both the value and difficulty of quantifying source-specific nitrogen transport in watersheds. Atmospheric emissions of nitrogenous compounds, an important source of nitrogen to coastal waters [Vitousek *et al.* 1997; Valigura *et al.* 1996;

Howarth *et al.* 1996; Fisher and Oppenheimer, 1991], are produced in both the electric utility and transportation sectors of the economy, and are currently under environmental regulation as air pollutants. Thus, better information on the effects of these compounds on coastal water quality will provide for a more comprehensive evaluation of an existing regulatory policy. The difficulty of quantifying the movement of atmospherically deposited nitrogen through watersheds is increased by the geographic complexity of the

sources, with some of the nitrogen falling directly on coastal and estuarine water surfaces and deposition occurring at varying rates throughout estuarine watersheds. Moreover, the use of different methods of assessment and the investigation of limited numbers of coastal watersheds in previous studies [Valigura *et al.* 1996] have prevented a consistent, comprehensive assessment of the importance of atmospheric sources to the nitrogen budgets of major coastal and estuarine ecosystems in the United States.

The general problem of tracing nitrogen flux through watersheds is complicated by the difficulty of establishing a spatially continuous mass balance between the in-stream flux of nitrogen, the rate of nitrogen supply from terrestrial and atmospheric sources, and the rate of removal due to denitrification and storage on the landscape and in stream channels. High quality stream monitoring data are frequently available for multiple sites within coastal watersheds, but these measure the integrated effects of nitrogen supply and loss processes operating continuously over the landscape and in stream channels. In this analysis, we use a watershed modeling technique [SPARROW-SPAtially-Referenced Regression On Watershed attributes; Smith et al. 1997; Alexander et al. 2000] that combines observations of stream water quality with spatial data on contaminant sources and watershed characteristics to separately estimate the quantities of nitrogen delivered to streams and the outlets of watersheds from point and diffuse sources. To provide a spatially consistent assessment of nitrogen flux from atmospheric as well as terrestrial sources to coastal waters of the conterminous United States, we calibrated the model using data from a national set of monitored watersheds. This model was previously used to quantify nitrogen deliveries to coastal waters from atmospheric and other sources in the Mississippi River Basin [Alexander et al. 2000]. The model expands on a previous national application of the SPARROW method [Smith et al. 1997; see section 2 for details]. We applied the model to 40 of the 42 major coastal watersheds of the conterminous United States (see fig. 1 in Chapter 1) selected for analysis in this book (two of the 42 watersheds lacked sufficient data), based on the use of local data on nitrogen sources and watershed attributes. We also compared the results of the national SPARROW model with those of other national and regional watershed models to assist in evaluating the model predictions. The analysis is presented in six sections. Following the introduction, the methodology and data sources for calibrating the national model are described. Section three presents the estimated model parameters. The results for the 40 U.S. estuaries are presented and discussed in section four. Section five presents the results of a comparison of model predictions with those of other large-scale watershed models. Conclusions appear in the final section.

2. Model Description and Data Sources

2.1 Background

A variety of deterministic and statistical methods have been used to develop models of nitrogen transport from human and natural sources to coastal waters. The simplest deterministic approaches [Jaworski *et al.* 1992; Jordan and Weller, 1996; Howarth *et al.* 1996] provide a static accounting of nitrogen inputs (e.g., fertilizer application,

atmospheric deposition) and outputs (e.g., river export, crop removal). Where sources or sinks (e.g., denitrification in soils and streams, groundwater storage) cannot be measured, estimates are often determined as a difference between the, measured inputs and outputs. These simple mass balance models assume that loss processes operate equally on all sources and that the relative contributions of sources to coastal waters are proportional to nitrogen inputs to the watersheds. More complex deterministic models of nitrogen flux [e.g., Bicknell *et al.* 1997; Srinivasan *et al.* 1993; Whitehead *et al.* 1998] simulate nitrogen availability, transport, and attenuation processes according to mechanistic functions and describe both spatial and temporal variations in sources and sinks. A third approach [export coefficient method; e.g. Fisher and Oppenheimer, 1991; Delwiche and Haith, 1983] has been to apply the reported yields (flux per unit area) from small, homogeneous watersheds to the variety of land types contained within larger heterogeneous basins.

There are important limitations to these approaches. First, the reported yields for various land types are highly variable [Beaulac and Reckhow, 1982; Frink, 1991;

Johnson, 1992], reflecting variations in climatic conditions, nutrient supplies, and terrestrial and stream loss processes as well as methodological differences related to sampling, measurement, and statistical estimation. Thus, the extrapolation of land-use yields to unmonitored watersheds can produced imprecise and potentially biased estimates of export. A more refined version of the export coefficient method, which accounts for spatial variations in source inputs and landscape and climatic conditions, has been successfully applied to catchments in the U.K. [e.g., Johnes, 1996] although this approach typically requires considerable monitoring to calibrate and verify the model [Johnes and Heathwaite, 1997]. Second, there are potential inaccuracies in "scaling up" the results of catchment models and field-scale measurements to larger watersheds [Rastetter et al. 1992; Beaulac and Reckhow, 1982], which in addition may exclude the effects of changes in nitrogen loss rates with stream properties (see section 3). Knowledge of in-stream losses may be especially important in large watersheds to account for the quantities of nitrogen removed during the lengthy in-channel movement of water from upstream locations to coastal ecosystems. However, reported estimates of in-stream nitrogen loss show large variations, ranging from less than five percent to as much as 80 percent of the external inputs of nitrogen to streams. Although studies suggest the importance of many chemical and physical properties of streams on nitrogen loss [e.g., Seitzinger and Kroeze, 1998; Seitzinger, 1988; Howarth et al. 1996; Kelly et al. 1987; Behrendt, 1996; Rutherford et al. 1987], there is poor knowledge of how in-stream nitrogen loss varies over a range of river sizes.

Statistical approaches to modeling nitrogen flux in coastal basins have their origins in simple correlations of stream nitrogen measurements with watershed sources and landscape properties. Recent examples [Mueller et al. 1997; Jaworski et al. 1997; Peierls et al. 1991; Howarth et al. 1996] include regressions of coastal nitrogen flux on population density, atmospheric deposition, and agricultural sources. Simple correlative models consider sources and sinks to be homogeneously distributed in space, do not separate terrestrial from in-stream loss processes, and rarely account for the interactions between sources and watershed processes. In contrast to their deterministic analogs, which often have intensive data and calibration requirements, the simplest empirical

models have the advantage of being more easily applied at large spatial scales. An additional noteworthy advantage of the statistical approach is the ability to quantify errors in model parameters and predictions.

2.2 The SPARROW Model

The SPARROW model used in this application is a hybrid method for empirically estimating the quantities of nitrogen delivered from point and diffuse sources to streams and watershed outlets. A spatially referenced regression technique is used to estimate in-stream flux as an exponential function of the landscape and hydraulic characteristics of watersheds. Surface water flow paths are defined according to a digital network of rivers to which stream monitoring data, nutrients sources, and watershed characteristics are spatially referenced. In contrast to conventional regression-based watershed methods [e.g., Jaworski et al. 1997; Mueller et al. 1997, this approach uses a mechanistic structure to track nitrogen transport through watersheds. Estimation is accomplished by establishing a mass balance in streams and rivers between 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 aquatic systems (i.e., channels and reservoirs). By regressing in-stream nutrient flux on watershed attributes, these rates are simultaneously estimated such that an optimal mass balance is attained between the observed and predicted flux at multiple stream monitoring locations. The method treats monitored flux as an in-stream nitrogen source in nested (i.e., overlapping) watersheds, thereby providing accurate stream data and numerous intervening river segments and drainage areas to assist in estimating the rates of nitrogen supply and removal. The contributions of various types of nitrogen sources to streams (e.g., fertilizer use, livestock wastes, municipal point sources) are quantified in the procedure from data on the magnitude and location of the source inputs. Large spatial variability in the explanatory variables improves the ability of the technique to separate "true" spatial variations in sources and processes from random variations related to measurement error and unexplained environmental factors. The empirical method also provides estimates of the uncertainty (e.g., 90% confidence intervals) in model coefficients and predictions of flux.

The model of in-stream nitrogen flux (F_i) is developed for a set of watersheds containing a defined set of stream reaches to which stream monitoring data and data on nutrient inputs and watershed characteristics are spatially referenced (see diagram in figure 1). The in-stream flux at the downstream end of a given reach i is expressed as the sum of all monitored and unmonitored sources of nitrogen in the set of upstream reaches denoted by J(i). The defined set of upstream reaches for a given reach; accounts for nested watersheds in the monitoring network such that the set excludes reaches that are either located above or include monitoring stations upstream of reach i. An estimable version of the expression is written as

$$Fi = \left\{ \sum_{n=1}^{N} \sum_{j \in J(i)} S_{n,j} \beta_n \exp(-\alpha Z_j) \exp(-k' T_{i,j}) \right\} \epsilon i$$

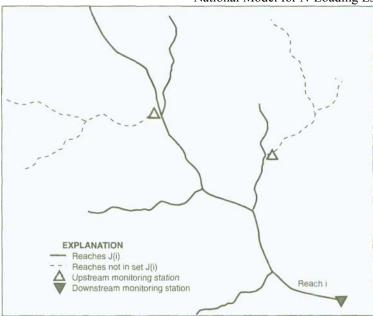


Figure 1. Schematic ofhydrologic network and monitoring stations modeled by SPARROW. Modified from Smith *et al.* (1997).

where $S_{n,j}$ is a measure of nitrogen mass from source n applied to the drainage of reach j, β_n is a source-specific coefficient, $\exp(-\alpha Z_i)$ is an exponential function describing the proportion of available nitrogen mass delivered to reach j as a function of land-to-water delivery coefficients (defined by vector α) and their associated terrestrial characteristics, Z_i , in the drainage to reach j, exp(-k'Ti,j) is the proportion of nitrogen mass present in reach j that is transported to downstream reach i as a function of a first-order rate of N loss (k' defined according to a vector of four discrete classes of channel size) per unit water travel time (Ti,j,), and E is a multiplicative error term assumed to be independent and identically distributed across independent sub-basins defined by the intervening drainage located between stream monitoring sites. The product of the land-to-water delivery function (and its associated coefficients) and the nonpoint-source coefficients quantifies the fraction of the source inputs that are delivered to rivers and streams. The delivery of nitrogen to streams is a function of several landscape characteristics of watersheds (Z_i), including soil permeability, stream density, and air temperature. The reciprocal of the land-to-water delivery (Z_i) was applied where a positive relation to in-stream flux is expected (e.g., stream density). The land-to-water delivery function is equal to one for point-source inputs. In estimating the source coefficients, upstream monitored inputs are treated as in-stream sources with their land-to-water delivery fraction, $\beta_n \exp(-\alpha Z_i)$, constrained to unity. We assume that the in-stream attenuation of nitrogen is identical for all sources according to the estimated rates of in-stream loss. The functional form of equation (1) dictates the use of nonlinear regression estimation methods. Coefficient estimation was performed on the log transforms of the summed

quantities and error term in equation (1) using non-linear least-squares estimation in the SAS procedure PROC MODEL [SAS, 1993]. Model residuals were examined for normality, constant variance, and nonlinear patterns to determine if regression assumptions were satisfied. Robust estimates of uncertainty of model parameters and predictions (standard errors and confidence intervals) were obtained in bootstrap analyses [Efron, 1982]. Bootstrap estimates of model parameter uncertainty were made by resampling with replacement (200 iterations) from the spatial set of stream monitoring flux data. Additional uncertainty related to unexplained variability in the model was included in bootstrap estimates of model predictions by resampling with replacement from the model residuals. In using the model to predict stream flux at unmonitored locations (reaches and watershed outlets), bootstrap estimates of residual errors were added to the predicted flux values at approximately the spatial scale of the monitoring station watersheds.

The methods and the version of the model applied here expand on a previous national application of SPARROW [Smith $et\ al.$ 1997] in several ways. First, we refined the empirical in-stream loss function to more accurately describe nitrogen attenuation in large rivers (> 283 m^3/s). Second, we detrended wet-fall measurements of atmospheric nitrogen deposition to reflect sources for the base year 1987 adjusted for long-term average precipitation, providing mean estimates of deposition consistent with the estimates of stream flux. Third, we calibrated the model using fewer stream monitoring stations (374 rather than 414), which were selected to provide contemporaneous records of nitrogen over a longer time period through 1992. Finally, we improved the estimates of uncertainty in the model predictions of source contributions to stream export by accounting for variability in the observed data that is unexplained by the model (i.e., residual errors).

2.3 In-Stream Monitoring Data

The SPARROW model was calibrated using U.S. Geological Survey (USGS) stream monitoring records of total nitrogen (TN) for the period 1978 to 1992 at 374 sites in the conterminous United States [see fig. 2; Alexander *et al.* 1998]. Estimates of TN flux in streams (*F*, in the spatial model in equation 1) were computed from periodically collected water-column measurements of total nitrogen (sum of nitrate-nitrite and kjeldahl nitrogen—ammonia plus organic N) and daily measurements of streamflow. Field sampling, analytical procedures, and quality assurance methods are performed according to USGS stream monitoring protocols [Alexander *et al.* 1998]. Water samples were collected for nutrient analysis according to a monthly to quarterly schedule. We estimated the mean TN flux at each monitoring station by applying conventional flux-estimation techniques [Cohn *et al.* 1989] to measurements of total nitrogen and daily streamflow, based on a log-linear model relating stream flux to streamflow, decimal time, and season of the year [Smith *et al.* 1997]. This method uses the more complete daily record of streamflow in estimating flux, and provides statistically unbiased estimates with greater precision than can be obtained from methods that rely on a simple averaging of the observed concentration and streamflow data. The number of samples at monitoring

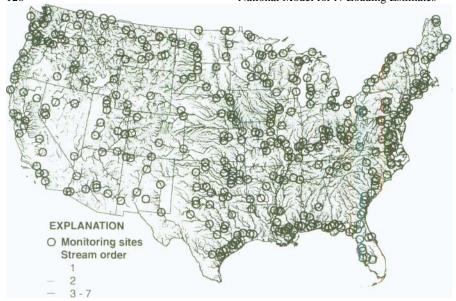


Figure 2. USGS stream monitoring locations and river reaches in the conterminous United States

sites was typically about 90 for the period of record (interquartile range from 75 to 105). These periodic samples provided relatively good coverage of the hydrograph; more than 75 percent of the stations have nutrient records that cover more than 95 percent of the streamflow events. Mean TN flux estimates are based on 1987 nitrogen inputs, adjusted for mean streamflow conditions for the years 1970-92. Source inputs for 1987 are representative of average inputs over at least the past two decades [Alexander *et al.* 2000]. Estimates of uncertainty in the mean flux (i.e., standard error of estimate) are determined according to methods in Gilroy *et al.* [1990]. Additional details of the flux-estimation method used in this analysis are provided in Smith *et al.* [1997]. Watersheds for the stations range in size from 80 to 2.9 million square kilometers (median=1 1,700;

interquartile range=3,000 to 34,000) with mean streamflow ranging from one to 18,500 cubic meters per second (median = 63; interquartile range = 20 to 217).

The estimates of mean TN flux at the 374 monitoring stations serve as the dependent variable in the SPARROW model. These estimates span approximately four orders of magnitude from 10^2 to slightly more than 10^6 kg day '. Yields at the stations range from 1.4 to 3,000 kg km⁻² yr⁻¹ (median=295 kg km⁻² yr⁻¹; interquartile range from 90 to 594 kg km² yr'). The highest TN yields occur in rivers of the midwestem and northeastern portions of the United States (see fig. 3) where the largest agricultural, atmospheric, and point source inputs to watersheds are typically found. The lowest yields are found in the western rivers where both nitrogen sources and runoff tend to be low relative to other areas of the United States. Uncertainties in the estimates of mean TN flux, based on the standard error of estimate expressed as a percentage of the mean (i.e., one standard deviation of the mean), range from about 2 to 19 percent (median = 6.2 %; interquartile

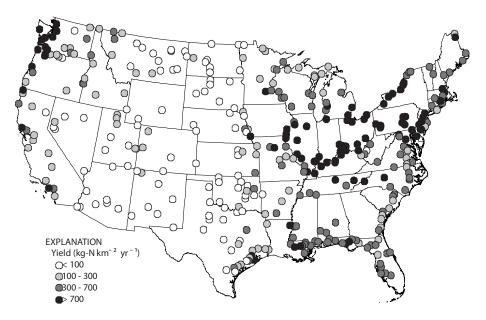


Figure 3. Mean total nitrogen yield at 374 USGS stream monitoring stations, 1978-1992. Estimates are adjusted to reflect 1987 sources and mean streamflow.

range=4.5 to 8.5%). Stations with standard errors greater than 20% of the station mean flux estimate (about 20 sites) were excluded from the spatial calibration of the SPARROW model to reduce the effects of measurement error. In general, prediction errors are lowest at those stations with the largest number of water-quality observations and in larger watersheds in the eastern portions of the United States, where less variable streamflow conditions occur.

2.4 Watershed Data

The spatial watershed data on nitrogen source inputs, physical characteristics of the landscape, and attributes of the digital stream network used in the SPARROW model have been previously described [Smith $et\ al.\ 1997$]. However, we modified the spatial estimates of wet deposition of nitrate by detrending the data according to the methods described in the subsequent section. For the base year 1987, we quantified nitrogen inputs to watersheds (the variable S $_{n\,j}$ in equation 1) for five major classes of sources including fertilizer use, municipal and industrial point sources, livestock wastes, runoff from nonagricultural land, and atmospheric deposition.

Data on the source inputs and terrestrial characteristics, available for nearly 20,000 land-surface polygons, were referenced to approximately 60,000 stream reaches in a digital stream network using conventional spatial disaggregation methods in a geographic information system [see Smith *et al.* 1997]. The surface water flow paths, defined according to a 1:500,000 scale digital network of rivers for the conterminous United States, cover nearly one million kilometers of channel, and are obtained from the USGS

version of the U.S. Environmental Protection Agency River Reach File 1 [ERF1;

Alexander *et al.* 1999; see fig. 2]. The river reach network provides the spatial framework in the model for relating in-stream measurements of flux at monitoring stations to landscape and stream channel properties in the watersheds above these stations. The median watershed size of the reaches is 82 km² with an interquartile range from 40 to 150 km². Stream attributes of the digital network include estimates of mean streamflow and velocity from which water time of travel is computed as the quotient of stream length and mean water velocity [Alexander *et al.* 1999].

2.4.1 Nitrate wet-deposition

Data from the National Atmospheric Deposition Program [NADP, 1993] were used to estimate the long-term mean annual wet deposition within RF1 reach watersheds in the conterminous United States. We used the approximately weekly measurements of nitrate at 188 monitoring sites with continuous records over the period of record from the early 1980s through 1993. We estimated a detrended mean annual nitrate deposition for the base year 1987 similar to that used to estimate total nitrogen flux in streams. This estimate gives the mean annual deposition at each monitoring site for 1987 under mean precipitation conditions.

We computed the detrended mean by adjusting observations of nitrate wet deposition for linear time trend over the period of record at each NADP site, based on a log-linear regression of nitrate deposition on time, precipitation, and season of the year (expressed as trigonometric functions of decimal time). Weekly measurements of nitrate deposition (d_b the product of concentration and precipitation) for the period of record were regressed on a set of five explanatory variables according to the form

$$\ln (d_1) = \lambda_0 + \lambda_1 \, n_i + \lambda_2 + \sin(2\pi n_i) + \lambda_3 \cos(2\pi n_i) + \lambda_4 \ln(p_i) + \lambda_4 (\ln(p_i))^2 + \epsilon_i (2)$$

where n_i is decimal time for the ith weekly observation, p_i is the ith weekly precipitation value, $\sin(2\pi n_i)$ and $\cos(2\pi n_i)$ are trigonometric functions that jointly estimate seasonal variations in deposition, λ are regression coefficients, ϵ_i is the sampling and model error assumed to be independent and identically distributed, and In is the natural logarithm. The detrended mean annual nitrate deposition for the base year 1987 at each NADP site (expressed as kg km⁻² yr⁻¹) is estimated as

$$\begin{array}{c} - & T \\ D = (T)^{-1} (\sum_{i=1}^{1} d_i \exp \left[\lambda_1 (t-n_i) - 0.5 \sigma^2 (t-n_i)^2 \right]^2) \\ \lambda_1 \end{array}$$

where t is the mid-year decimal value for 1987, $\sigma_{\lambda 1}$ is the standard error of the linear time model coefficient, and T is the number of observations. The models typically explained

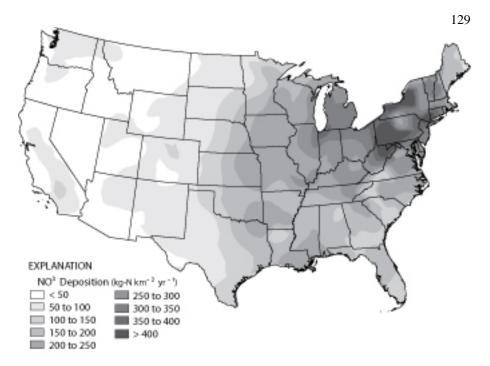


Figure 4. Mean annual nitrate wet deposition m the conterminous United States, 1980-1993. The spatially interpolated estimates at NADP sites are adjusted to reflect 1987 deposition and mean precipitation.

from 55 to 70 percent (median R-squared = 64 percent) of the observed temporal variability in nitrate wet deposition. Model residuals exhibited acceptable adherence to regression assumptions.

Spatially continuous values of nitrate wet-deposition were estimated for the United States by linearly interpolating the mean annual nitrate deposition estimates for the 188 NADP monitoring locations through application of the Triangulated Irregular Network (TIN) method in Arc/Info [ESRI, 1996]. The resulting nitrate wet-deposition surface for the conterminous United States is illustrated in figure 4 for a contour interval of 50 kg km⁻² yr⁻¹. The estimates of nitrate wet deposition span more than two orders of magnitude ranging from lows of less than 10 kilograms per square kilometer in the West to hundreds of kilograms per square kilometer in the East. A distinct pattern of high nitrate deposition occurs over the Ohio Valley and extends into the northeastern United States. The atmospheric deposition mass of contoured surface polygons (10 kg km⁻² yr⁻¹ intervals) was apportioned to the watersheds of individual RF1 reaches according to the ratio of the watershed, reach length to the total reach length in deposition polygons [see Smith *etal.* 1997].

Estimates of nitrate wet deposition for the 40 estuarine drainage areas, computed as the mean of the estimated inputs to reach watersheds, range in magnitude from 0.5 to 3.4 kg ha⁻¹ yr⁻¹ (i.e., 50 to 340 kg km⁻² yr⁻¹; see table 1). These estimates show a strong spatial correlation (r = 0.97) with the values of nitrate wet deposition [Meyers *et al.* this volume]

National Model for N-Loading Estimates

TABLE 1. Nitrate wet deposition in the drainages of major estuaries of the conterminous United States.

| Number | Drainage | 3.4 337 - |
|---------|--|--|
| Reaches | Area (km ²) | Mean Wet Deposition (kg ha''' yr ¹) |
| | | iiu ji) |
| 30 | 3093 | 1.87 |
| | | 2.02 |
| | | 2.86 |
| 9 | | 2.34 |
| | | 2.13 |
| | | 2.55 |
| 1 | | 2.79 |
| | | 3.12 |
| | | 3.33 |
| | | 3.06 |
| | | 3.03 |
| | | 3.44 |
| 1 | | 2.81 |
| 2 | | 2.68 |
| | | 3.10 |
| 12,5 | 101,150 | 5.10 |
| 219 | 24.584 | 2.18 |
| 423 | | 1.99 |
| 597 | | 1.56 |
| 151 | | 1.40 |
| 6 | | 1.14 |
| 509 | 36,797 | 1.77 |
| 3 | | 1.45 |
| | | |
| 57 | 9,146 | 1.53 |
| 2 | 957 | 1.53 |
| 41 | 6,556 | 1.58 |
| 79 | 15,254 | 1.44 |
| 425 | | 1.63 |
| 1219 | 115,339 | 1.71 |
| 302 | 44,448 | 2.17 |
| 20 | 6,151 | 2.26 |
| 6 | 4,095 | 2.25 |
| 68 | 11,174 | 1.86 |
| 378 | 54,081 | 1.78 |
| 519 | 63,158 | 1.65 |
| 518 | | 0.98 |
| 231 | 44,853 | 0.93 |
| 40 | 9,065 | 1.14 |
| 20 | , | 1.15 |
| | * | |
| 829 | 108,943 | 0.46 |
| 572 | 31,166 | 0.77 |
| | 14 27 1 525 508 12 26 250 1 2 1293 219 423 597 151 6 509 3 57 2 41 79 425 1219 302 20 6 68 378 519 518 231 40 20 20 20 20 20 20 20 20 20 2 | 30 3093 11 2378 89 12,906 9 2,524 14 3,654 27 4,613 1 2,192 525 40,289 508 41,629 12 1,649 26 3,705 250 32,373 1 726 2 847 1293 164,156 219 24,584 423 46,340 597 40,604 151 12,358 6 2,253 36,797 3 1,525 57 9,146 2 957 41 6,556 79 15,254 425 52,236 1219 115,339 302 44,448 20 6,151 6 4,095 68 11,174 378 54,081 519 63,158 518 117,565 231 44,853 40 9,065 20 7,179 |

TABLE 2. SPARROW total nitrogen model coefficients based on a regression of stream nitrogen flux at 374 river monitoring stations on watershed characteristics. Refer to the methods and equation 1 for an explanation of the model form and coefficients.

| Model Parameters | Coefficient Units | Bootstrap Coefficient | Lower 90% CI ^b | Upper 90% CI ^b |
|---|--------------------------------------|--------------------------|------------------------------|------------------------------|
| 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 | $^{\circ}\mathrm{F}^{-\mathrm{l}}$ | 0.017 | 0.009 | 0.023 |
| Soil permeability | hr. cm ⁻¹ | 0.036 | 0.024 | 0.049 |
| Drainage area per stream length ^a | km ⁻¹ | 0.043 | 0.017 | 0.063 |
| In-stream loss rate c, k | | | | |
| $k_1 (Q < 28.3 \text{ m}^3 \text{ s}^{-1})$ | day ⁻¹ | 0.455 | 0.344 | 0.579 |
| $k_2 (28.3 \text{ m}^3 \text{ s-1} < Q < 283 \text{ m}^3 \text{ s-}^1)$ | day ⁻¹ | 0.118 | 0.063 | 0.176 |
| $k_3 (283 \text{ m}^3 \text{ s}^{-1} < Q < 850 \text{ m}^3 \text{ s}^{-1})$ | day ⁻¹ | 0.051 | 0.007 | 0.092 |
| $k_4 (Q > 850 \text{ m}^3 \text{ s}^{-1})$ | day ⁻¹ | 0.005 | 0.000 | 0.019 |
| R-Squared | | 0.881 | | |
| Mean square error | | 0.435 | | |
| Number of observations | | 374 | | |

a Variable enters the model in reciprocal form (see Smith et al. 1997).

used in the land-use based model in this volume (also see comparisons in the final chapter). SPARROW estimates are within about 20 percent of these values in most of the watersheds (the ratio of Meyers *et al.* estimates to SPARROW estimates typically range from 1.17 to 1.30; median=1.22). Estimates of nitrate wet deposition according to Meyers *et al.* are also based on NADP data, but include an additional three years of observations (1994-96) and result from the use of different estimation methods.

3. National SPARROW Model Estimates

3.1 Calibration of the Model

Correlating stream TN flux with the spatially referenced data on nitrogen sources and watershed characteristics, we find that a model consisting of 12 explanatory variables explains approximately 88 percent of the variability in the 374 observations of mean annual TN flux. The explanatory variables and estimated coefficients for the TN model are presented in table 2. Estimates of uncertainty in the fitted coefficients in table 2 are

b Minimum bootstrap confidence intervals (CI).

c In-stream loss rates fit separately for stream reaches with mean

streamflow (Q) corresponding to the indicated intervals.

expressed as 90 percent confidence intervals based on the bootstrap estimation procedure. Five types of nitrogen sources and three land-to-water delivery factors were statistically significant. The rates of in-stream total nitrogen removal are estimated according to four streamflow classes (table 2).

A comparison of model predictions with observed values of TN flux and yield is shown in figure 5. The differences between the observed and predicted values (i.e., model residuals) indicate acceptable adherence of the errors to the model assumptions. The model residuals are approximately normal with relatively constant variance, and no systematic linear or curvilinear patterns are visible. There is some evidence of a slight overestimation of flux in watersheds with exports less than about 1,000 kg day⁻¹ (fig. 5a). Comparisons of observed and predicted yield, which adjust for the effect of basin area giving unit expressions similar to concentration, provide a more stringent evaluation of model performance. Somewhat larger variation occurs in the predicted TN yields than for flux (fig. 5b), but acceptable correlation (R-squared=0.80) is observed between the predicted and observed yield values. Moreover, relatively constant variance occurs in the residuals throughout the range of yield values suggesting the lack of any systematic biases in the estimation of TN yield (fig. 5b). Based on an examination of the distribution of the absolute percent differences between the observed and predicted yields, about half of the predictions are found to be within at least 32 percent of the observed values. A quarter of the predictions are within at least 15 percent of the observed values, whereas a quarter exceed the observed values by more than 61 percent. Only 10 percent of the model predictions exceed the observed values by more than 100 percent. Overall, the TN model performs well enough to serve as a relatively accurate predictive tool for use in estimating TN flux and yield in unmonitored watersheds. Moreover, model residuals are generally well behaved, and would be expected to provide reasonably accurate estimates of the uncertainty associated with the model predictions.

3.2 Model Parameter Estimates

The product of the nitrogen-source coefficients (table 2) and exponential land-to-water delivery function estimate the nitrogen mass that is made available from nitrogen sources and delivered to streams. The quantities of nitrogen delivered to streams may reflect the contributions from other sources not explicitly measured by the input variables, such as dry deposition, fixation by crops, crop imports, and groundwater, as well as the effects of terrestrial processes (e.g., soil denitrification, crop exports, climate, conservation tillage, and subsurface storage and transport). In addition to direct runoff of applied fertilizers, the "fertilizer" source may include fixed nitrogen in leguminous crop residues and other soil nitrogen associated with cropland. Nonagricultural nonpoint sources include nitrogen inputs quantified by the model intercept scaled for nonagricultural land, and thus include remaining nitrogen inputs unaccounted for by other sources in the model. Nonagricultural sources include nitrogen entering streams via runoff and subsurface flows from wetlands as well as from urban, range, forested, and barren lands. Nitrogen from forested and range lands may include biotic fixation (Jordan and Weller, 1996). The model coefficient for point sources (to which the land-to-water delivery function is

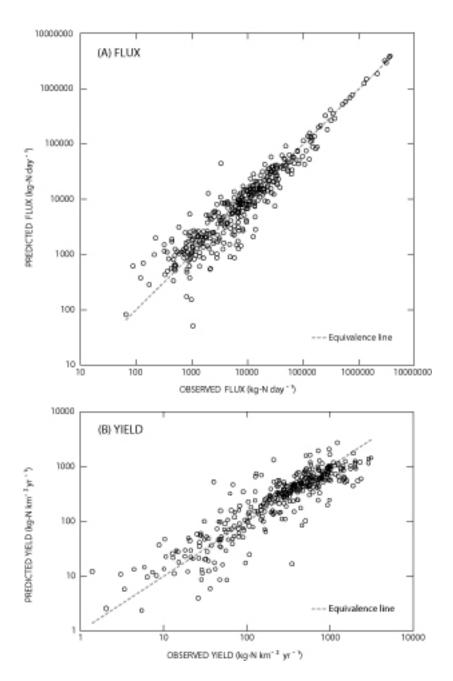


Figure 5. SPARROW model predictions at 374 stream monitoring stations in relation to the observed mean total nitrogen (A) flux and (B) yield.

not applied) is less than unity. This likely reflects model adjustments for declines in point source loads between the 1970s (the time period of the input data) and the 1987 base year used to estimate stream flux [Smith, *et al.* 1997]. The model estimates of municipal and industrial point-source loadings to streams expressed per capita (based on the sewered population) have a median of 3.8 kg-N person⁻¹ (interquartile range of 1.7 to 7.1 kg-N person⁻¹). This compares favorably with literature estimates of per capita rates for residential wastewater effluent ranging from 2.2 to 7 kg-N person⁻¹ [Thomann, 1972; USEPA, 1980].

In estimating atmospheric nitrogen contributions, we used wet-deposition measurements of nitrate nitrogen as input to the model, and excluded ammonia deposition to minimize the double accounting of agricultural sources of nitrogen in the input term [Howarth et al. 1996]. The land-to-water delivery fraction for wet nitrate deposition (product of the deposition coefficient and the exponential land-to-water delivery function) exceeds unity, and is consistent with our assumption that atmospheric sources include additional contributions from wet deposition of ammonium and organic nitrogen and dry deposition of inorganic nitrogen, which are not reflected by the input variable. The model would be expected to account for these additional sources to the extent that they are correlated with the measured inputs of nitrate. Although estimates of these other depositional forms are not widely available for the United States, available estimates for the estuarine watersheds [Meyers et al. this volume] indicate that wet nitrate deposition is highly correlated (r=0.78) with dry plus ammonium and organic wet deposition (dry is based on separate dry-fall monitoring data and model predictions). Estimates of the ratio of total (dry plus wet) deposition to nitrate wet deposition for the estuarine watersheds [Meyers et al. this volume] range from 3.2 to 4.0 with an average of 3.6 (uncertainties in estimates of total deposition may exceed a factor of two). In addition, estimates of total NOy deposition (dry plus wet oxidized forms) in the United States have been reported to range from 2 to 3 times the nitrogen in wet deposition [Fisher and Oppenheimer, 1991].

Landscape processing and transport of nitrogen to rivers are modeled as an exponential function of several physical descriptors of the watersheds, including air temperature, soil permeability, and stream density (table 2). Temperature and soil permeability are inversely correlated with stream flux; the former providing possible evidence of a large-scale temperature-related denitrification effect [Seitzinger, 1988] and the latter suggesting greater long-term storage of nitrogen or permanent loss in areas of higher soil permeability (possibly via soil denitrification or immobilization by soil microbes). Drainage density is positively correlated with in-stream nitrogen flux suggesting that watersheds with higher stream densities deliver sources more efficiently to channels;

stream density may also reflect the influence of climate on nitrogen flux.

The removal of total nitrogen in rivers is estimated as a function of four first-order loss rates (expressed per unit water travel time) that vary inversely with channel size. The SPARROW loss rates span nearly two orders of magnitude from 0.455 per day of travel time in small streams to 0.005 in large rivers (table 2). The magnitude of the loss rates and their inverse relation to channel size are consistent with literature estimates of in-stream nitrogen loss based on a recent re-analysis of mass balance and denitrification

studies [Alexander *et al.* 2000]. Benthic denitrification is expected to be the principle loss process reflected by these rates based its importance in watershed studies [Howarth *et al.* 1996]. The physical storage and release of particulate nitrogen, such as on flood plains and in reservoirs, may also contribute to these rates. The decline in the rate of nitrogen loss (per unit of travel time) with increasing stream size suggests that the physical and biochemical processes responsible for the removal of nitrogen in streams become progressively less effective with increases in channel depth [Alexander *et al.* 2000].

3.3 Model Predictions of Nitrogen Export

We applied equation 1 and the SPARROW coefficient estimates to data on nitrogen source inputs, landscape attributes, and channel time of travel to predict TN export from the five source types at the outlets of the 60,000 reach watersheds in the RF1 network. The predictions include estimates of the TN export for the entire watershed above each reach and predictions for each separate reach watershed (i.e., "local" or incremental TN export), excluding the flux from upstream basins. We estimated the fraction of the stream export contributed by each nitrogen source (i.e., source share) as the ratio of each source's TN export to the total TN export. The SPARROW predictions include estimates of the mean and standard error based on the application of the bootstrap procedure.

Predictions of TN export (expressed as yield; kg km⁻² yr⁻¹) at the outlets of the 60,000 reach watersheds (inclusive of the entire drainage area) range over four orders of magnitude with a median of 530 kg km⁻² yr⁻¹ (interquartile range from 318 to 804 kg km⁻² yr⁻¹). The spatial distribution of yields is similar to that observed for the monitoring sites; the highest yields occur in streams of the midwestem and northeastern states with the lowest yields predicted for streams in the western states. Model predictions are summarized for the 40 coastal watersheds in the following section.

As an initial evaluation of the accuracy of the model predictions of flux, we compared the predictions of "local" TN export (in units of yield; kg ha⁻¹ yr⁻¹) for basins having a predominant land use type with yields reported in the literature for similar land uses (see table 3). Because of the large variability in the watershed characteristics, the SPARROW yields span as much as an order of magnitude or more for certain sources. Although the RF1 reach watersheds are typically larger and contain more diverse sources than those studied in the literature, the SPARROW yields for the most homogeneous watersheds lie well within the range of yields reported for various land uses and sources in North American watersheds (table 3). Watersheds dominated by urban sources and agriculture (crop and pasture land) have the largest nitrogen yields, whereas the quantities of nitrogen exported from watersheds with forest and range lands are one-tenth to one-quarter of these yields. Variability in the literature yields can be attributed to factors other than land cover, including nitrogen supply, climate, landscape characteristics, and stream properties [Ritter, 1988; Novotny and Olem, 1994; Frink, 1991; Beaulac and Reckhow, 1982].

TABLE 3. SPARROW estimates of total nitrogen (TN) export from major land types compared to literature estimates. SPARROW estimates are reported for TN exported from watersheds associated with individual stream reaches as defined by the digital river network for the conterminous United States.

| Watershed Distribution of TN Yield Exported from SPARROW Watersheds ^a | | | | | | | | |
|--|--------|-----------|-----------|------------------------|-------------------|------------------|----------|---|
| Land- | | | | (kg ha ⁻¹ y | r ⁻¹) | | | Exports ^b |
| Cover | | | | | | | | (kg ha ⁻¹ yr ⁻¹) |
| Type | | | | | | | | |
| | Number | 10^{th} | 25^{th} | Medium | 75 th | 90 th | Range of | Range of |
| | | | | | | | Values | Values |
| | | | | | | | | |
| Crops | 203 | 12.1 | 17.4 | 22.2 | 29.3 | 35.5 | 2.2-42.4 | 0.8-79.6 |
| Pasture | 19 | 9.5 | 14.4 | 16.8 | 19.2 | 20.3 | 8.5-20.8 | 0.1-30.8 |
| Forest | 17 | 1.8 | 3.6 | 4.5 | 6.1 | 7.4 | 1.8-11.2 | 0.1-10.8 |
| Range | 58 | 1.3 | 2.1 | 2.9 | 4.0 | 5.4 | 0.4-7.4 | 1.5-6.8 |
| Urban | 22 | 4.6 | 20.0 | 31.6 | 87.0 | 95.2 | 3.6-175 | 1.6-38.5 |

^a The land-cover types represent the following percentages of the land area in SPARROW watersheds: crops (>90%), pasture (>85%), forest (>95%), range (100%), urban (>75%). ^b

4. Nitrogen Export and Sources in the Estuarine Watersheds 4.1

Total Nitrogen Export

The national SPARROW model estimates of mean total nitrogen flux exported from the estuarine drainage areas are presented in table 4. Included in table 4 are the mean estimates of the percentage of nitrogen export contributed by the five major types of sources. Nitrogen flux estimates are standardized by the area of the drainage basin and expressed as export or yield (kg km⁻² yr⁻¹) to adjust for differences in area among the estuarine watersheds. Units can be converted to kg ha⁻¹ yr⁻¹ according to $100 \text{ kg km}^{-2} = 1 \text{ kg ha}^{-1}$. Estimates of uncertainty in export are given in table 5.

Mean TN yield varies by about a factor of sixty among the estuarine watersheds, ranging from about 38 to 2,500 kg km⁻² yr⁻¹. Yields more commonly vary from about 250 to 650 kg km⁻² yr⁻¹ as reflected by the interquartile range (difference between the 75th and 25th percentiles). The median TN yield is 450 kg km⁻² yr⁻¹. Distinct regional differences exist in the nitrogen export from the estuarine watersheds among the four major geographically contiguous sections of coastline (see table 4). The highest values of export (and the largest range) are observed in the North Atlantic (NA) region (median=520 kg km⁻² yr⁻¹), which includes coastal waters from Maine south to the Chesapeake Bay. Four watersheds display yields greater than 1,000 kg km⁻² yr⁻¹ in this region, and include the Massachusetts Bay, Narragansett Bay, Delaware Bay, and the

b Total nitrogen export taken from ranges reported in literature reviews (Beaulac and Reckhow, 1982; Frink, 1991; Ritter, 1988). The export reported for "range" is for grasslands in Oklahoma, U.S. (Ritter, 1988).

Hudson River. Exports of total nitrogen from the estuarine watersheds in the South Atlantic (SA) region are among the lowest and display the narrowest range of values among the regions. The median export is one half of that of the NA region and most watershed exports range from 100 to about 450 kg km⁻² yr⁻¹. The highest export in the SA region is found in the Pamlico Sound watershed. Although the median export for watersheds in the Gulf of Mexico region (470 kg km⁻² yr⁻¹) is similar to that of the NA, exports are generally lower than those in the NA (range of 60 to 720 kg km⁻² yr⁻¹; interquartile range from 300 to 500 kg km⁻² yr⁻¹). The highest yields range from 500 to about 700 kg km⁻² yr⁻¹ in the Gulf region, and occur in the watersheds of the Upper Laguna Madre, TX, Mobile Bay, West Mississippi Bay, and Calcasieu Lake. Both Pacific watersheds show moderately high yields of about 600 kg km⁻² yr⁻¹.

4.2 Atmospheric Nitrogen

The mean quantities of atmospheric nitrogen in rivers exported from the estuarine watersheds range over nearly two orders of magnitude from 4 to 326 kg km⁻² yr⁻¹ (see table 4). Estimates typically vary from 30 to 110 kg km⁻² yr⁻¹, based on the interquartile range. When expressed as a percentage of the total nitrogen flux, atmospheric nitrogen is estimated to represent from 4 to 35% of the total nitrogen mass exported from the estuarine watersheds (see table 6; fig. 6). Atmospheric contributions typically range from 10% to slightly more than 20% of the stream nitrogen exports.

Similar to the geographic patterns observed for total nitrogen export, the NA region shows the greatest range and highest magnitude of atmospheric export and percentage contributions to stream export (median=120 kg km⁻² yr⁻¹; see fig. 7). In nearly one half of the estuarine watersheds in the NA region (7 watersheds), atmospheric nitrogen represents more than 20% of the total stream export, including the watersheds of the Long Island Sound (41%), the Merrimack (27%), Hudson (25%), and Chesapeake Bay (28%). Although the median contribution of atmospheric nitrogen to stream export is similar for the NA and SA regions (-17%), the atmospheric shares are somewhat lower in the SA region, typically ranging from 14% to 22%; none of the atmospheric exports are larger than about 100 kg km⁻² yr⁻¹ in this region. In the Gulf of Mexico region, atmospheric nitrogen represents a slightly smaller share of the stream export than in the SA region. The median percentage share (14%) is slightly lower than in the SA region, and atmospheric nitrogen exports are commonly less than about 80 kg km⁻² yr⁻¹. However, there are several estuarine watersheds where atmospheric nitrogen is estimated to contribute from 20 to 27% of the total river exports, including Mobile Bay, W. Mississippi Sound, Terrebonne Bay, and Sabine Lake. The larger exports in these watersheds correspond to larger inputs of atmospheric deposition in this area of the southeastern United States as reflected in the estimates of wet deposition of nitrate (fig. 4; table 1). Despite higher wet deposition of nitrate in the more populated watersheds of the western United States (fig. 4), atmospheric nitrogen represents a very small percentage of the total nitrogen exports from the two Pacific watersheds (5% in San Francisco Bay, 12% in the Puget Sound).

TABLE 4. Total nitrogen export from sources in the drainages of major estuaries of the conterminous United States. Mean annual export (i.e., yield) is in units of kg km $^{-2}$ yr $^{-1}$.

| Watershed/Estuary | Total | Atmos- | Point | Fertilizer | Live- | Nonagric. |
|-------------------------------------|-------|----------|----------|------------|---------|-----------|
| | | phere | Sources | | stock | Nonpoint |
| North Atlantic | | | | | | |
| 1. Casco Bay | 386 | 85 | 51 | 22 | 20 | 207 |
| 2. Great Bay | 382 | 34 | 89 | 19 | 16 | 223 |
| 3. Merrimack River | 445 | 123 | 90 | 22 | 17 | 193 |
| 3. Worldinger River | | | | | | |
| 4. Massachusetts Bay | 2,489 | 98 | 2,193 | 27 | 10 | 161 |
| 6. Buzzards Bay | 135 | 16 | 85 | 13 | 3 | 18 |
| Narragansett Bay | 1,051 | 110 | 656 | 59 | 27 | 200 |
| 8. Gardiners Bay | 38 | 4 | 4 | 14 | 0 | 15 |
| Long Island Sound | 881 | 304 | 148 | 79 | 60 | 289 |
| 10. Hudson River/ Raritan | 1,277 | 326 | 516 | 96 | 71 | 267 |
| Bay | | | | | | |
| 11. Barnegat Bay | 864 | 160 | 367 | 84 | 10 | 243 |
| 12. New Jersey Inland | 515 | 136 | 115 | 104 | 9 | 151 |
| Bays | | | | | | |
| 13. Delaware Bay | 1,332 | 296 | 467 | 225 | 122 | 222 |
| 14. Delaware Inland Bays | 174 | 16 | 39 | 33 | 76 | 10 |
| <u></u> | 174 | 10 | 37 | 33 | 70 | 10 |
| 15. Maryland Inland Bays | 243 | 20 | 105 | 33 | 67 | 18 |
| 16. ChesapeakeBay | 814 | 228 | 62 | 171 | 173 | 179 |
| | | | | | | |
| South Atlantic | 751 | 109 | 31 | 353 | 126 | 132 |
| 17. Pamlico Sound | | | | | - | - |
| 18. WinyahBay | 428 | 80 | 18 | 164 | 57 | 109 |
| 19. Charleston Harbor | 107 | 23 | 12 | 18 | 11 | 43 |
| 20. St. Helena Sound | 138 | 24 | 2 | 37 5 | 6 | 68 |
| 22. St. Catherinefe / | 234 | 47 | 4 | 3 | 2 | 176 |
| Sapelo S. | 457 | 105 | 16 | 133 | 67 | 137 |
| 23. Altamaha River | 89 | 7 | 11 | 60 | 2 | 9 |
| 24. Indian River | | , | 11 | 00 | _ | |
| Gulf of Mexico | 270 | 40 | _ | 212 | 10 | 62 |
| 25. Charlotte Harbor | 370 | 48 35 | 7 176 | 212 33 | 42 | 62 |
| Sarasota Bay | 309 | 51 | | 227 | 8 53 | 56 44 |
| 27.Tampa Bay | 481 | - | 106 | 93 | | |
| 28. Apalachee Bay | 281 | 40 | 15 | | 22 | 111 |
| Apalachicola Bay | 479 | 70 | 35 | 185 | 55 | 134 |
| 30. Mobile Bay | 515 | 122 | 13 | 109 | 82 | 188 |

| TABLE 4. Continued. |
|---------------------|
|---------------------|

| 31. West Mississippi Sound | 508 | 131 | 47 | 105 | 80 | 145 |
|----------------------------------|-----|-----|-----|-----|-----|-----|
| 32. Barataria Bay | 541 | 49 | 322 | 46 | 9 | 115 |
| 33. Terrebonne/ Timbalier Bay | 229 | 61 | 21 | 11 | 1 | 135 |
| 34.Calcasieu Lake | 616 | 107 | 134 | 163 | 36 | 176 |
| 35. Sabine Lake | 351 | 71 | 23 | 72 | 60 | 124 |
| 36. Galveston Bay | 468 | 62 | 183 | 99 | 45 | 79 |
| 37. Matagorda Bay | 123 | 17 | 3 | 68 | 17 | 19 |
| 38. Corpus Christi | 56 | 5 | 11 | 26 | 4 | 9 |
| Bay | | | | | | |
| Upper Laguna | 717 | 83 | 12 | 226 | 106 | 290 |
| Madre | | | | | | |
| 40. Lower Laguna | 566 | 42 | 52 | 381 | 17 | 73 |
| Madre Pacific | | | | | | |
| 41. San Francisco | 585 | 32 | 74 | 244 | 82 | 154 |
| Bay | | | | | | |
| 42.Puget Sound | 677 | 80 | 96 | 103 | 86 | 313 |

4.3 Other Source Contributions

In comparison to atmospheric sources, the other sources generally contribute greater quantities of nitrogen to the estuaries. A comparison of the percentage contributions to stream export of the five source categories estimated by SPARROW is shown in figure 6.

Agricultural sources (i.e., fertilizer use, livestock wastes) represent the largest single source of nitrogen in the estuarine watersheds, accounting for more than about a third of the nitrogen in the stream export of most basins. Agricultural source contributions to river export range from 2 to 70% of the nitrogen, although the contributions more commonly range from about 13 to 50% of the stream exports in most watersheds based on the interquartile range (median=33%). Fertilizer-related sources may include leaching of mineralized soil nitrogen and N fixation by crops. Livestock wastes represent about one-third of the total agricultural nitrogen contributions to streams.

Geographic variations in agricultural contributions to river export are shown in figure 8. Agricultural contributions are highest in the SA region where a median of 42% is observed for the estuarine watersheds. In two of the watersheds, the Pamlico Sound and Indian River, more than 60% of the stream export is derived from agricultural sources. In the Gulf of Mexico region, agricultural contributions are similar in magnitude to those in the SA region (median of 38%), and represent at least 50% of the stream export in six of the watersheds (Charlotte Harbor, Tampa Bay, Apalachicola Bay, Matagorda Bay, Corpus Christi Bay, and Lower Laguna Madre; see table 6). In the Pacific region, agricultural sources represent 61% of the nitrogen export in the San Francisco watershed and 28% in the Puget Sound. By contrast to the other regions, watershed exports to estuaries in the NA region contain much less agricultural nitrogen (typically less than 15% of the river exports). The highest contributions in the NA region are found in

TABLE 5. Estimates of uncertainty in total nitrogen export from sources in the drainages of major estuaries of the conterminous United States. Estimates of uncertainty are based on the standard error, expressed as a percentage of the mean export, and reflect error in the model coefficients and unexplained variability in the observed data (i.e., model residuals).

| Watershed/Estuary T | otal | Atmos- phere | Point Sources | Fertilizer | Live- stock | Nonagric. Nonpoint |
|----------------------|------|-----------------|------------------|------------|----------------|-----------------------|
| North Atlantic | | | | | | |
| 1. Casco Bay | 64 | 46 | 46 | 33 | 61 | 21 |
| 2. Great Bay | 63 | 56 | 45 | 34 | 61 | 20 |
| 3. Merrimack | 46 | 45 | 44 | 28 | 58 | 27 |
| River | | | | | | |
| 4. Massachusetts | 71 | 83 | 10 | 96 | 104 | 74 |
| Bay | | | | | | |
| 6. Buzzards Bay | 75 | 68 | 27 | 49 | 80 | 49 |
| 7. Narragansett 57 | | 61 | 23 | 42 | 71 | 42 |
| Bay | | | | | | |
| 8. Gardiners Bay | 111 | 54 | 113 | 17 | 64 | 19 |
| 9. Long Island 29 | | 41 | 44 | 29 | 59 | 30 |
| Sound | | | | | | |
| 10. Hudson River/ | 34 | 48 | 34 | 35 | 63 | 37 |
| Raritan Bay | | | | | | |
| 11. Barnegat Bay | 72 | 50 | 30 | 33 | 72 | 31 |
| 12. New Jersey | 49 | 44 | 43 | 24 | 63 | 29 |
| Inland Bays | | | | | | |
| 13. Delaware Bay | 29 | 48 | 33 | 30 | 59 | 31 |
| 14. Delaware | 83 | 102 | 76 | 66 | 86 | 121 |
| Inland Bays | | | | | | |
| 15. Maryland | 81 | 83 | 43 | 64 | 91 | 83 |
| Inland Bays | | | | | | |
| 16. Chesapeake | 19 | 45 | 51 | 26 | 53 | 27 |
| Bay | | | | | | |
| South Atlantic | | | | | | |
| 17. Pamlico Sound | 31 | 49 | 53 | 17 | 53 | 21 |
| 18. Winyah Bay | 26 | 47 | 53 | 19 | 53 | 21 |
| 19. Charleston | 35 | 47 | 48 | 21 | 53 | 24 |
| Harbor | | | | | | |
| 20. St. Helena | 46 | 50 | 59 | 18 | 57 | 19 |
| Sound | | | | | | |
| 22. St. Catherines / | 73 | 53 | 74 | 49 | 80 | 15 |
| Sapelo S. | | | | | | |
| 23. Altamaha River | 30 | 47 | 57 | 23 | 53 | 22 |
| 24. Indian River | 87 | 58 | 77 | 17 | 69 | 36 |
| Gulf of Mexico | | | | | | |
| 25. Charlotte | 55 | 48 | 57 | 16 | 56 | 26 |
| Harbor | | | | | | |
| 26. Sarasota Bay | 72 | 59 | 26 | 41 | 68 | 39 |
| 27.Tampa Bay | 37 | 52 | 49 | 21 | 56 | 25 |
| 28. Apalachee Bay | 40 | 49 | 53 | 19 | 55 | 21 |
| 20. Aparachee Day | 40 | 77 | 55 | 1) | 55 | <u>~ 1</u> |

TABLE 5. Continued.

| 29. | Apalachicola | 25 | 49 | 53 | 19 | 54 | 20 |
|-----|----------------|----|----|----|----|----|----|
| | Bay | | | | | | |
| 30. | Mobile Bay | 20 | 46 | 57 | 22 | 52 | 21 |
| 31. | West | 28 | 44 | 50 | 24 | 53 | 25 |
| | Mississippi | | | | | | |
| | Sound | | | | | | |
| 32. | Barataria Bay | 58 | 59 | 22 | 38 | 70 | 38 |
| 33. | Terrebonne / | 64 | 46 | 55 | 33 | 64 | 22 |
| | Timbalier Bay | | | | | | |
| 34. | Calcasieu Lake | 40 | 47 | 43 | 22 | 57 | 23 |
| 35. | Sabine Lake | 27 | 47 | 52 | 22 | 51 | 23 |
| 36. | Galveston Bay | 32 | 55 | 36 | 29 | 57 | 33 |
| 37. | Matagorda Bay | 32 | 50 | 58 | 17 | 56 | 21 |
| 38. | Corpus Christi | 48 | 55 | 54 | 23 | 58 | 24 |
| | Bay | | | | | | |
| 39. | Upper Laguna | 54 | 52 | 60 | 19 | 54 | 17 |
| | Madre | | | | | | |
| 40. | Lower Laguna | 64 | 56 | 55 | 14 | 63 | 32 |
| | Madre | | | | | | |
| | Pacific | | | | | | |
| 41. | San Francisco | 26 | 54 | 50 | 19 | 53 | 20 |
| | Bay | | | | | | |
| 42. | Puget Sound 30 | | 52 | 53 | 24 | 52 | 18 |
| | | | | | | | |

watersheds of the eastern Maryland shore, where livestock wastes contribute as much as 30 to 40% of the total nitrogen in river exports.

Non-agricultural diffuse sources are estimated to contribute slightly less to watershed exports than agricultural sources. The median contribution to watershed exports is 27% with most contributions ranging from 17 to 40%, based on the interquartile range (fig. 6). The percentage contribution is larger in the estuarine watersheds of the South Atlantic region than in other regions. Contributions from this source are based on the model intercept scaled for nonagricultural land area in the watersheds, and thus represent nitrogen inputs not explicitly accounted for by the other model sources. Nonagricultural sources may include nitrogen in the runoff from urban, forested, range, wetlands, and barren lands. Nitrogen runoff from forested and range lands may include biotic fixation. In watersheds of the western Gulf region and the Pacific region, nonagricultural diffuse sources are highly associated with range lands which constitute a predominant land type. Groundwater nitrogen, which generally reflects a more constant and less variable component of the nitrogen flux in watersheds, may also be included in this source category. Groundwater may reflect contributions from older waters originating from a variety of local and regional sources.

Municipal and industrial point sources represent the largest share of the nitrogen in stream exports in about one quarter of the estuarine watersheds, including one-half of the North Atlantic watersheds and several watersheds in the Gulf region. In the North Atlantic watersheds dominated by point sources, the shares represent from 35 to 88% of the nitrogen in stream export. The highest point source shares are found in the

TABLE 6. Source contributions to total nitrogen export in percent from the drainages of major estuaries of the conterminous United States.

| Watershed/Estuary | Atmosphere | Point Sources | Fertilizer | Livestock | Nonagric. Nonpoint |
|-------------------------------------|------------|---------------|------------|-----------|-----------------------|
| North Atlantic | | | | | |
| Casco Bay | 22 | 13 | 6 | 5 | 54 |
| 2. Great Bay | 9 | 23 | 5 | 4 | 58 |
| Merrimack River | 28 | 20 | 5 | 4 | 43 |
| Massachusetts Bay | 4 | 88 | 1 | 0 | 6 |
| 6. Buzzards Bay | 12 | 63 | 9 | 2 | 14 |
| 7. Narragansett Bay | 10 | 62 | 6 | 3 | 19 |
| 8. Gardiners Bay | 11 | 10 | 38 | 1 | 41 |
| 9. Long Island Sound | 35 | 17 | 9 | 7 | 33 |
| 10. Hudson River/ Raritan Bay | 26 | 40 | 8 | 6 | 21 |
| 11. Bamegat Bay | 19 | 43 | 10 | 1 | 28 |
| 12. New Jersey | 26 | 22 | 20 | 2 | 29 |
| Inland Bays | | | 20 | - | |
| 13. Delaware Bay | 22 | 35 | 17 | 9 | 17 |
| 14. Delaware Inland | 9 | 22 | 19 | 44 | 6 |
| Bays | , | | 17 | | Ü |
| 15. Maryland Inland Bays | 8 | 43 | 14 | 28 | 7 |
| 16. Chesapeake Bay | 28 | 8 | 21 | 21 | 22 |
| South Atlantic | 20 | 0 | 21 | 21 | 22 |
| 17. Pamlico Sound | 14 | 4 | 47 | 17 | 18 |
| 18.WinyahBay | 19 | 4 | 38 | 13 | 26 |
| 19. Charleston | 22 | 11 | 17 | 10 | 40 |
| Harbor | 22 | 11 | 1, | 10 | 40 |
| 20. St. Helena Sound | 18 | 2 | 27 | 5 | 49 |
| 22. St. Catherines / | 20 | 2 | 2 | 1 | 75 |
| Sapelo S. | -0 | - | _ | - | , , |
| 23. Altamaha River | 23 | 3 | 29 | 15 | 30 |
| 24. Indian River | 8 | 12 | 68 | 2 | 10 |
| Gulf of Mexico | | | | | |
| 25. Charlotte Harbor | 13 | 2 | 57 | 11 | 17 |
| 26. Sarasota Bay | 11 | 57 | 11 | 3 | 18 |
| 27. Tampa Bay | 11 | 22 | 47 | 11 | 9 |
| 28. Apalachee Bay | 14 | 5 | 33 | 8 | 40 |
| 29. Apalachicola Bay | 15 | 7 | 39 | 11 | 28 |
| 30. Mobile Bay | 24 | 3 | 21 | 16 | 37 |
| 31. West Mississippi | 26 | 9 | 21 | 16 | 29 |
| Sound | -0 | | | 10 | |
| 32. Barataria Bay | 9 | 60 | 8 | 2 | 21 |
| 33.Terrebonne/ | 27 | 9 | 5 | 1 | 59 |
| Timbalier Bay | <i></i> | | - | - | -/ |
| 34. Calcasieu Lake | 17 | 22 | 26 | 6 | 29 |
| 35. Sabine Lake | 20 | 7 | 21 | 17 | 35 |
| 36. Galveston Bay | 13 | 39 | 21 | 10 | 17 |
| | | | | | |

TABLE 6. Continued.

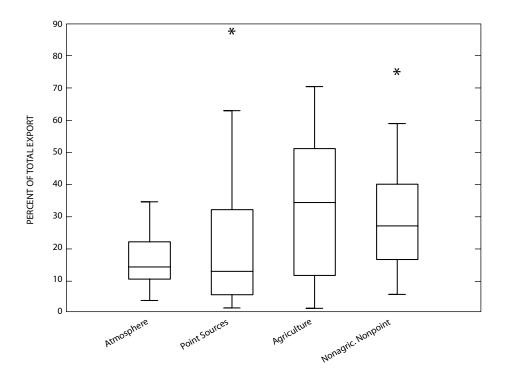
| 37. Matagorda Bay | 14 | 2 | 55 | 14 | 15 | |
|---------------------------|----|----|----|----|----|--|
| 38. Corpus Christi Bay | 10 | 19 | 47 | 8 | 16 | |
| 39. Upper Laguna Madre | 12 | 2 | 31 | 15 | 40 | |
| 40. Lower Laguna Madre | 8 | 9 | 67 | 3 | 13 | |
| Pacific | | | | | | |
| 41. San Francisco Bay | 5 | 13 | 42 | 14 | 26 | |
| 42.Puget Sound 12 | | 14 | 15 | 13 | 46 | |

Massachusetts Bay (88%), Buzzards Bay (63%), and Narragansett Bay (62%). The largest point-source shares in the Gulf region include Sarasota Bay (57%), Barataria Bay (60%), and Galveston Bay (39%). In most watersheds, point sources are similar to or less than the contributions from the atmosphere (fig. 6), and typically represent less than 15% of the nitrogen in stream export.

4.4 Estimates of Uncertainty

Estimates of uncertainties in the mean nitrogen exports and source shares are presented in table 5. The estimates of the standard error (one standard deviation), expressed as a percentage of the mean, reflect two sources of uncertainty: variability in the estimates of the model coefficients and unexplained variations in the data according to the model predictions (as described by the model residuals). Estimates of the portion of the residual error associated with each of the source shares is computed by assuming that each source's share of the ijesidual error is proportional to the source's share of mean total nitrogen export.

The standard errors on total export among the estuarine watersheds range from 19% to 117% of the mean. One half of the mean exports have standard errors less than 40%. The standard errors of the individual source contributions are typically larger. For example, errors in atmospheric nitrogen export range from 41% to 102%; one half of the exports have standard errors less than 50%. The magnitude of the uncertainty in the estimates of nitrogen export is inversely related to drainage basin size (see fig. 9). This relation reflects the intrinsic effect of averaging on error reduction. Model residual errors are systematically assigned to the predictions of stream export at the outlets of hydrologic cataloging units (HCU) to account for variability in stream flux that is unexplained by the model. Estuarine watersheds with large drainage areas have a correspondingly greater number of HCUs. Thus, the larger watersheds have lower error because the cancellation of errors increases with the number of errors averaged. The standard errors in the estimates of nitrogen export range from 19% to 50% of the mean in watersheds above 10,000 square kilometers in size (60% of the estuarine watersheds are larger than this size). Standard errors range from 50% to 70% of the mean in watersheds between 2,000



SOURCE TYPE

Figure 6. Contributions of sources to total nitrogen export from major estuarine drainage areas of the United States. Each box graphs the watershed quartiles, with lower and upper edges representing the 25th and 75th percentiles, respectively. The midline plots the median. The upper and lower whiskers are drawn to the watershed value within +/- 1.5 times the interquartile range. Watershed values exceeding three times the IQR appear as a "*". Agriculture is the sum of the fertilizer and livestock waste sources.

and 10,000 square kilometers in size (20% of the estuarine watersheds fall within this size range). In watersheds smaller than 2,000 square kilometers, the standard errors are typically greater than 80% of the mean. Estimates of nitrogen export and source contributions for these watersheds have the lowest reliability. Examples include the estuarine watersheds of Gardiners Bay (111%), Delaware Inland Bays (83%), Maryland Inland Bays (81%), and mdian River (87%).

4.5 Landscape and Aquatic Attenuation

Summary statistics related to nitrogen attenuation on the landscape and in streams are shown for the estuarine watersheds in table 7. The land-to-water delivery index in table 7 is an indicator of the relative proportion of a diffuse source input that is transported to streams as a function of the model's landscape properties, including soil permeability, air

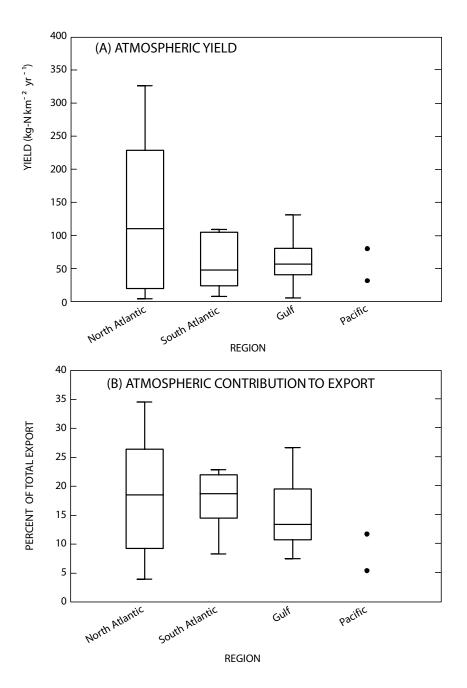


Figure 7. The atmospheric contributions to total nitrogen export from major estuarine drainage areas of the United States by region; (A) atmospheric yield, (B) percentage of total nitrogen export. See table 4 for description of estuaries and regions. Each box graphs the watershed quartiles, with lower and upper edges representing the 25th and 75th percentiles, respectively. The midline plots the median. The upper and lower whiskers are drawn to the watershed value within +/-1.5 times the interquartile range. The dots give statistics for the two Pacific watersheds.

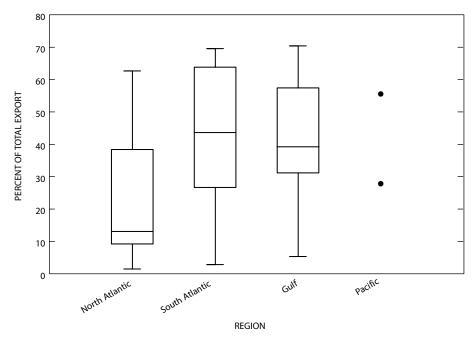


Figure 8. The contributions of agriculture to total nitrogen export from major estuarine drainage areas of the United States by region. Agriculture is the sum of fertilizer and livestock waste source contributions. Each box graphs the watershed quartiles, with lower and upper edges representing the 25th and 75th percentiles, respectively. The midline plots the median. The upper and lower whiskers are drawn to the watershed value within +/- 1.5 times the interquartile range. The dots give statistics for the two Pacific watersheds.

temperature, and drainage density. The product of the land-to-water delivery index and the model's diffuse source coefficient and input data quantify the fraction of the measured source inputs that is delivered to streams (see equation 1). Although the NA region displays the largest range in values of the land-to-water delivery index, the values are typically lower in the watersheds of this region than in other regions (median=0.13 compared with 0.20 or larger in other regions). This indicates that higher proportions of the nitrogen inputs are typically removed in this region as a function of the landscape properties of the watersheds. The higher permeability of soils in the watersheds of the NA region appears to account for an important portion of this effect. Low values of the index are also observed in several Florida watersheds where higher soil permeabilities and temperatures are generally found.

The mean quantities of atmospheric nitrogen delivered to streams in the estuarine watersheds (expressed per unit of watershed area) are predicted to range from 0.05 to 4.7 kg $\rm ha^{-1}~yr^{-1}$ (table 7). These quantities range from a few percent to nearly 30 percent of the total (dry plus wet) atmospheric inputs estimated by Meyers *et al.* [this volume].

The quantities of nitrogen removed in streams and reservoirs of the estuarine watersheds, expressed as a percentage of the quantity of nitrogen delivered to stream

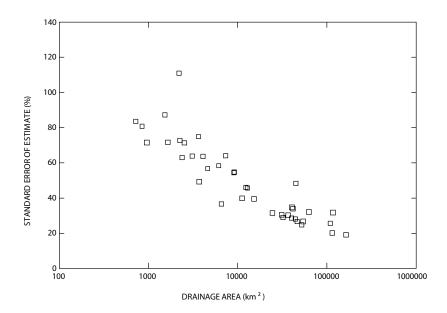


Figure 9. The standard error of estimate for mean total nitrogen yield in relation to estuarine drainage area.

channels, range from nparly zero to about 90 percent (table 7). The percentage removal more typically ranger from about 5 to 44%, based on the interquartile range (median=25%). In the smallest estuarine watersheds, especially those containing fewer than 10 reaches, in-stream losses of nitrogen are negligible. We find that in-stream losses are much lower in watersheds of the NA region, where a median of 7% of the nitrogen is removed. This reflects the effect of the shorter water travel times in this region (i.e., 0.2 to 3.5 days), which are typically one quarter to one half of the travel times estimated for the estuarine watersheds in other regions. The estuarine watersheds of the SA region show the largest range, of in-stream losses spanning from negligible quantities to nearly 60% (median=44%). [The loss percentages for the estuarine watersheds of the Gulf region (median=42%) are similar to those in the SA region, although the percentages typically span a narrower range from about 27 to 53%. There are notable differences in the percentage of in-s^ream loss between the Gulf estuarine drainages in the east and those in the west that relate to both water travel time and channel size differences. Several of the western Gulf estuarine watersheds (Galveston Bay, Matagorda Bay, and Corpus Christi Bay) have large drainage areas with long water travel times (10 to 25 days) and small rivers with relatively low flow, which collectively result in large in-stream nitrogen losses (60 to 90%). By contrast, much smaller in-stream nitrogen losses (<45%) are observed in the eastern Gulf watersheds characterized by generally smaller drainage sizes and higher streamflow.

TABLE 7. Total nitrogen (TN) delivery to streams and in-stream nitrogen loss rates for the drainages of major estuaries of the conterminous United States. "N" denotes a negligible instream total nitrogen loss.

| Watershed/Estuary | Land-to- Atmospheric Water TN Delivered Delivery to Streams ^b Index ^a (kg ha ⁻¹ yr ⁻¹) | | In-Stream TNLoss ^c (% of stream inputs) | Mean Water Time of Travel (days) | |
|--|---|------|--|---|------|
| North Atlantic | | | | | |
| 1. Casco Bay | 0.1 | 9 1 | .07 | 19 | 1.3 |
| 2. Great Bay | 0.1 | 1 0 | .33 | N | 0.4 |
| 3. Merrimack River | 0.1 | 8 1 | .55 | 19 | 3.1 |
| 4. Massachusetts Bay | 0.1 | 3 0 | .92 | 7 | 0.5 |
| 6. Buzzards Bay | 0.0 | 3 0 | .15 | N | 0.2 |
| 7. Narragansett Bay | 0.1 | 4 1 | .19 | 4 | 0.7 |
| 8. Gardiners Bay | 0.0 | 2 0 | .05 | N | 0.2 |
| Long Island Sound | 0.2 | 6 4. | 36 | 27 | 4.0 |
| 10. Hudson River/Raritan Bay | 0.2 | 8 4. | 67 | 21 | 4.5 |
| 11. Barnegat Bay | 0.1 | 3 1. | 60 | N | 0.6 |
| 12. New Jersey Inland Bays | 0.1 | 3 1 | .64 | 16 | 1.0 |
| 13. Delaware Bay | 0.2 | 6 4. | 00 | 21 | 3.5 |
| 14. Delaware Inland Bays | 0.0 | 5 0 | .14 | N | 0.2 |
| 15. Maryland Inland Bays | 0.0 | 5 0 | .15 | N | 0.2 |
| Chesapeake Bay | 0.2 | 5 3 | .69 | 37 | 4.9 |
| South Atlantic | | | | | |
| 17. Pamlico Sound | 0.2 | 4 2 | .18 | 44 | 4.5 |
| 18.WinyahBay | 0.2 | 3 2. | 00 | 60 | 6.3 |
| Charleston Harbor | 0.2 | 5 2 | .14 | 89 | 8.3 |
| 20. St. Helena Sound | 0.1 | 8 0 | .48 | 44 | 4,0 |
| 22. St. Catherines/Sapelo S. | 0.1 | 4 0 | .42 | N | 0.5 |
| 23. Altamaha River | 0.2 | 2 2 | .22 | 53 | 6.6 |
| 24. Indian Rivte | 0.0 | 2 0 | .07 | N | 0.1 |
| Gulf of Mexico | | | | | |
| 25. Charlotte Harbor | 0.0 | 8 0 | .67 | 37 | 1.8 |
| 26. Sarasota Bay | 0.0 | | .29 | N | 0.5 |
| 27. Tampa Bay | 0.0 | | .70 | 26 | 1.3 |
| 28. Apalachee Bay | 0.1 | | .61 | 44 | 2.6 |
| 29. Apalachicola Bay | 0.2 | | .23 | 43 | 5.5 |
| 30. Mobile Bay | 0.2 | | .00 | 44 | 7.9 |
| 31. West Mississippi Sound | 0.2 | | .08 | 42 | 4.2 |
| 32. Barataria Bay | 0.1 | | .72 | 35 | 1.7 |
| 33. Terrebonne/Timbalier Bay | 0.1 | | .66 | 8 | 0.8 |
| 34. Calcasieu Lake | 0.2 | | .69 | 33 | 2.9 |
| 35. Sabine Lake | 0.2 | | .49 | 56 | 6.2 |
| 36. Galveston Bay | 0.2 | | .77 | 61 | 9.9 |
| 37. Matagorda Bay | 0.2 | | .86 | 81 | 24.9 |
| 38. Corpus Christi Bay | 0.2 | 0 0 | .95 | 91 | 17.9 |

TABLE 7. Continued.

| 39. Upper Laguna Madre | 0.20 | 1.07 | 23 | 1.4 | |
|------------------------|------|------|----|-----|--|
| 40. Lower Laguna Madre | 0.15 | 0.62 | 45 | 1.6 | |
| Pacific | | | | | |
| 41. San Francisco Bay | 0.25 | 0.63 | 45 | 5.3 | |
| 42.Puget Sound | 0.26 | 0.87 | 11 | 1.7 | |

^a The mean land-to-water delivery index, computed according to $\exp(-\acute{\mathbf{C}} Zj)$ in equation 1, is an indicator of the relative proportion of a diffuse source input that is transported to streams as a function of the specified landscape properties (the product of the land-to-water delivery index and the model's diffuse source coefficient and associated input data quantify the fraction of the source input that is delivered to streams—see equation 1). The delivery index is the product of the delivery indices for temperature, permeability, and drainage density.

4.6 Geographic Origins of Atmospheric Nitrogen

An understanding of the origins of nitrogen entering coastal ecosystems depends not only on knowledge of the relative contributions of the sources, but also on the location of sources in the watershed. This information is useful in evaluating and designing efficient nitrogen management strategies that provide the greatest reduction in nitrogen inputs to coastal waters in response to the least amount of control effort. Such information is complementary to other information, such as the costs of control technologies, that is necessary to assess the efficiencies of alternative strategies. Spatial variations in the quantities of atmospheric nitrogen delivered to an estuary will depend significantly on the location and magnitude of sources within the contributing watershed. As an illustration of this, we describe estimates of atmospheric nitrogen delivered to the Chesapeake Bay from inland watersheds. These estimates are derived from a previous application of the SPARROW model in the Chesapeake Bay watershed [CB SPARROW; Preston and Brakebill, 1999]. CB SPARROW is similar to the national SPARROW in terms of nitrogen sources and model structure, and is described in section 5.2.

One simple approach to examine the importance of nearby versus more distant watershed sources of atmospheric nitrogen is to consider the nitrogen contributions of watersheds to the Bay in relation to their river distance upstream of the estuary. Accordingly, we arranged the atmospheric nitrogen exports that are delivered to the Bay from the incremental drainage areas of the 1,400 interior reaches in ascending order by their river distance from the estuary. We summed these delivered exports over increasing

Atmospheric delivery to streams is computed as the mean of model predictions for watershed reaches. The predictions of atmospheric TN delivery reflect uncertainties in model coefficients, but do not include uncertainties related to the unexplained variability in the observed data (i.e., model residuals). Note that the predictions of atmospheric export in table 4 include uncertainties based on the model coefficients and residuals, and therefore, may exceed stream deliveries of atmospheric TN in cases where in-stream losses are reported to be small.

^c The in-stream loss is the mean percentage of the total quantity of nitrogen delivered to watershed reaches from all sources that is removed in streams. Note that for some estuaries the in-stream loss of atmospheric TN differs from that for total sources because of differences in the locations of sources.

river distances from the Bay and expressed the sum as a percentage of the total atmospheric nitrogen that enters the estuary. Figure 10a displays a map of the spatial pattern of the cumulative percentage of nitrogen that is delivered to the Bay from watersheds located over increasing distances from the estuary. In the accompanying plot (fig. 10b), we find that, when watersheds are considered in relation to their distance from the Bay, the per unit area contributions of atmospheric nitrogen to the estuary are largest in watersheds that comprise from 20 to about 50% of the total Bay drainage area. For these areas of the watershed, the curve describing the cumulative percentage of atmospheric nitrogen delivered to the Bay ranges from about 25 to nearly 55 percent, and plots above the line of equivalence for cumulative drainage area. Over this range, the contributions of nitrogen flux to the Bay are approximately 10 percent higher than the percentage of contributing drainage area (the percentage is about 20 percent for all sources as shown in figure 10b). This disproportionate contribution of nitrogen in relation to drainage area generally reflects the combined effect of relatively high atmospheric deposition and the efficient transport of nitrogen from areas in proximity to the Bay, especially from areas in the vicinity of large rivers. 'The areas include the lower portions of the Susquehanna, Potomac, and James rivers, which are characterized by short water travel times (per unit channel length) and low rates of in-stream nitrogen loss (per unit water travel time).

The quantities of atmospheric nitrogen delivered to the Bay can also be examined in terms of the per unit area contribution or "delivered yield" of inland watersheds (see fie. 11). The delivered yield adjusts the nitrogen export from inland watersheds by their drainage area, and thus, can be used to identify inland watersheds that contribute the largest nitrogen mass per unit area to the Bay. The higher values of delivered atmospheric yield in figure 11 a show the effects of high atmospheric deposition and the more efficient transport of nitrogen from watersheds in the vicinity of large rivers. Watersheds in proximity to the Susquehanna, Potomac, and James rivers and their largest tributaries transport a disproportionately larger quantity of nitrogen per unit area (by a factor of 2 to 3) than many of the watersheds draining smaller streams in proximity to the Bay. This spatial pattern is attributed to the lower rates of in-stream nitrogen loss and the shorter water travel times (per unit channel length) in large rivers as compared to small streams. The importance of channel size to the efficiency of nitrogen transport and delivery to coastal waters was previously noted in the Mississippi River Basin [Alexander et al. 2000]. We find that inland watersheds in the northern portions of the Bay watershed generally receive the highest atmospheric deposition, but have low to moderate delivered yields. The water travel times are generally much longer for these watersheds increasing the opportunities for in-stream processes to remove nitrogen from the water column.

5. Comparisons with Other Large-Scale Spatial Models

One of the objectives of this chapter is to compare the SPARROW model predictions of total nitrogen flux in streams with other model estimates available at large spatial scales. There are no other national-scale nutrient models, but the agricultural model

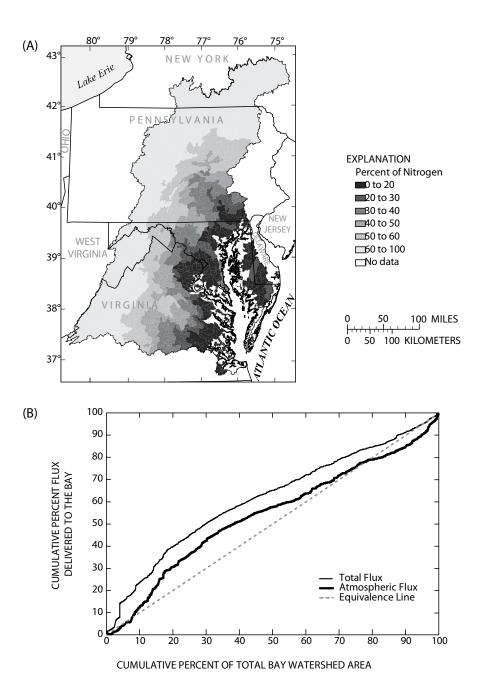


Figure 10. Cumulative percentage of the total nitrogen entering the Chesapeake Bay that originates from the outlets of interior watersheds as a function of river channel distance from the Bay: (A) map of atmospheric nitrogen by watershed; (B) total and atmospheric flux in relation to cumulative drainage area. The nitrogen export and drainage area are accumulated for incremental watershed areas defined by 1,400 reach segments.

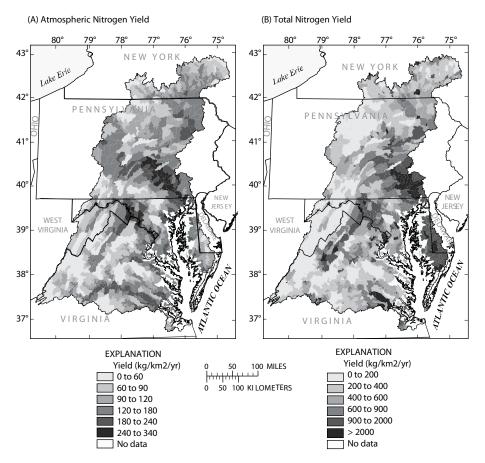


Figure 11. Mean total nitrogen yield delivered to the Chesapeake Bay from the outlets of interior basins of the watershed: (A) atmospheric nitrogen; (B) total nitrogen. Nitrogen yields are estimated for incremental watershed areas defined by 1,400 reach segments.

SWAT [Soil and Water Assessment Tool; Srinivasan *et al.* 1993; Arnold *et al.* 1990] has been recently used to simulate watershed exports of total nitrogen from 1,400 of the 2,077 hydrologic cataloging units of the central and eastern United States as part of the HUMUS (Hydrologic Unit Modeling of the United States) Project. SWAT is the only deterministic model applied at this large spatial scale. We compared SPARROW predictions to those of the SWAT model for the 1,400 hydrologic units and for 38 of the 42 estuarine watersheds selected for analysis in this book for which SWAT predictions could be obtained. We also compared results of the national SPARROW model with **those** available for two regional models applied in the 164000 square kilometer Chesapeake Bay watershed: the HSPF [Hydrologic Simulation Program Fortran; Bicknell *et al.* 1997] hydrologic model and a recently developed SPARROW model calibrated with monitoring data from 79 locations in the Chesapeake Bay watershed.

Although comparisons of these large-scale models are possible, there are certain noteworthy limitations. First, the SWAT and HSPF models differ from SPARROW in the methods of describing nitrogen supply, terrestrial and aquatic losses, and in the spatial and temporal scales of measurement and prediction. For example, many of the nitrogen inputs in the models reflect different time periods and are based on different assumptions, such as the nitrogen inputs for fertilizer and livestock wastes in SWAT. Also, atmospheric nitrogen *is* not accounted for in the SWAT model, making it necessary **to** adjust this term to allow comparisons. Second, stream monitoring data were not available at the outlets of the hydrologic cataloging unit watersheds. Thus, SWAT and SPARROW model predictions could not be directly compared with independent observations of stream nitrogen flux (many of the monitoring stations in the SPARROW calibration data set are located near the outlets of hydrologic cataloging units [Alexander *et al.* 1998]; model accuracy is described in section 3.1).

5.7 Comparisons with SWAT

5.1.1 The SWAT agricultural model

The hydrologic simulation model, SWAT, is a predictive tool used as part of the Hydrologic Unit Model for the United States (HUMUS) Project [Srinivasan *et al.* 1993; Arnold *et al.* 1990], a regional and national effort to simulate the hydrologic cycle, and its related impacts on the natural resources, in the 2,077 major watersheds in the 48 conterminous. SWAT combines the features of the nonpoint-source watershed model, SWRRB [Simulator for Water Resources in Rural Basins; Williams *et al.* 1985; Arnold *et al.* 1990] and a flow routing model for channels and reservoirs, ROTO [Routing Outputs to Outlet; Arnold *et al.* 1995]. The SWAT model is physically based, operates on a daily time step, and simulates the effects of management changes in agricultural practices on stream water quality.

The major model components for subbasins in SWAT include hydrology, weather, sedimentation, soil temperature, crop growth, nutrients, and agricultural management. Hydrology includes surface runoff, percolation, lateral subsurface flow, groundwater flow, evapotranspiration, snow melt, channel routing, transmission losses and pond/reservoir storage. The weather variables are precipitation, air temperature, solar radiation, wind speed, and relative humidity. Estimates of the long-term mean precipitation are based on a 30 year period, 1960-89. Surface runoff volume from non-urban areas is estimated by using the Soil Conservation Service (SCS) curve number procedure and from urban areas making use of the USGS Urban Storm Runoff Loading Model [Tasker and Driver, 1988]. Sediment yield from rural watersheds is estimated for each subbasin with the Modified Universal Soil Loss Equation (MUSLE) from which the organic nitrogen content and yield are estimated. Crop use of nitrogen is based on a supply and demand approach that allows uptake to continue until the daily demand is met or nitrogen is depleted. Crop growth and nitrogen use are simulated as a function of estimates of crop conversions of energy to biomass and rates of crop harvest. The amounts of nitrate contained in runoff, lateral flow, and percolation are estimated as the products of the volume of water and the mean concentration. Soil denitrification is a

function of temperature and organic carbon and soil water content. The model considers mineralization sources from the fresh active organic N pool in the crop residue of each soil layer and microbial biomass and the stable organic N pool in the soil humus. The export of total nitrogen (TN) from each land use type in a subbasin is estimated as the sum of the nitrate in surface and sub-surface runoff and organic-N in sediment. Total nitrogen export at the hydrologic unit outlet is obtained by summing the routed subbasin yields of nitrate, nitrite, organic-N and ammonium (NH4-N). Stream routing is based on the height and width of rectangular channels during two-year return flows. A neural network model [Muttiah et. al. 1997] estimates channel dimensions from modeling unit elevations and drainage areas. A storage coefficient method [Arnold et. al. 1995] routes water through streams and reservoirs, adding flows and inputting measured data and point sources. In-stream nutrient kinetics are controlled by QUAL-2E routines that use estimates of reach time of travel [Arnold et. al. 1995]. County-based municipal and industrial point sources used in the SPARROW model were accounted for in SWAT;

aquatic attenuation of the point sources was applied according to SWAT estimates of channel and reservoir decay. The rate coefficients that describe watershed processes in SWAT are based on field-scale measurements; no formal model calibration is employed **to** adjust the rate coefficients and match model predictions with observed stream monitoring data.

Topography and channel topology are determined from 1:250,000 scale Digital Elevation Model (DEM) data. Watershed boundaries are from 1:500,000 scale State hydrologic unit maps. Land use/land cover (LULC) data are from the USGS LULC data 250 by 250 meters at 1:250,000 scale derived from aerial photography and LANDSAT images during the 1980s, updated with 1990 census population for urban areas. Cropland areas are from county-level data of the Census of Agriculture, and soils properties are from the State Soil Geographic (STATSGO) database. Model predictions of nutrient flux are made for hydrologic cataloging units, where up to 21 crop and soil polygons may exist (approximately 200 km² per polygon). The hydrologic response unit for estimating water balances and process interactions is defined according to these polygons. Reservoir nutrient attenuation is modeled as an aggregate component within these spatial units based on reservoir hydraulic properties.

5.1.2 Results of Comparisons with SWAT

We compared SPARROW model predictions of total nitrogen export with SWAT predictions for 1,430 hydrologic cataloging units (HCU) in the eastern and central portions of the United States covering 12 of the 18 major hydrologic regions [Seaber *et al.* 1987; regions 1 through 12). These estimates reflect nitrogen mass contributed by the total drainage area above each HCU, inclusive of the nitrogen contributions of all upstream HCUs. We also compared the "local" yield estimates from both SPARROW and SWAT models for the 1,430 HCUs; these reflect nitrogen mass contributed from sources within each HCU independent of inflows from upstream HCUs. Finally, we compared model predictions of total nitrogen export for 38 of the 42 estuarine drainages selected for analysis in this chapter (SWAT estimates were not computed for the two Pacific estuaries). SWAT predictions of export were computed for the estuarine

watersheds by apportioning the HCU estimates of TN export to the estuarine watersheds in proportion to the HCU drainage area common to both.

Because the SWAT model does not include nitrogen inputs from atmospheric deposition, adjustments to the model predictions were necessary to allow comparisons with SPARROW; the SPARROW estimate of atmospheric nitrogen flux was added to the SWAT prediction of total nitrogen flux for each watershed. To minimize the effect of drainage area on comparisons of model predictions of TN flux, comparisons were made on TN yield (flux per unit area), adjusting the flux estimates for the drainage area of the hydrologic cataloging units used in each of the models. The model estimates of drainage area differ by less than 10 percent for more than 97 percent of the hydrologic units.

The results of the model comparisons are shown for the "total" hydrologic unit TN yield in figure 12a and for the "local" hydrologic unit yield in figure 12b. The model predictions are closely correlated for both the total (r=0.67) and local (r=0.83) yields. SPARROW predictions tend to be consistently larger than those for HUMUS over the range of yields with somewhat larger differences for the local yields. The distribution of the ratios of SPARROW to SWAT total yield has a median of 1.4 with an interquartile range from 0.9 to 2.1. Fewer than 20 percent of the ratios are smaller than 0.55 or larger than 3.0. Uncertainties in SPARROW predictions of total yield, based on the standard error of prediction, are typically 45 to 66 percent (median=59 percent), and scale inversely with watershed area (see discussion in section 4.4). The distribution of the ratios of SPARROW to SWAT local yield has a median of 2.3 with an interquartile range from 1.6 to 3.4. Fewer than 20 percent of the ratios are smaller than 1.1 or larger than 4.7. Uncertainties in SPARROW predictions of local yield typically range from 60 to 70 percent (median=65 percent). Estimates of uncertainties are not available for the SWAT model predictions.

Predictions of total nitrogen yield exported from the estuarine drainages are presented in figure 13. There is ^ positive correlation (r=0.55) among the model predictions over the range of yields. In contrast to the comparisons for the hydrologic units, SPARROW predictions of yield are consistently smaller (in about 2/3's of the watersheds) than those for SWAT. In addition, differences in model predictions are slightly smaller for the estuarine watersheds than for the HCU comparisons of total yield (fig. 13a). The distribution of the ratio of SPARROW to SWAT total yield has a median of 0.73 with an interquartile range from 0.5 to 1.3. Fewer than 20 percent of the ratios sire smaller than 0.3 or larger than 1.5. Uncertainties in SPARROW predictions of total yield in these watersheds, based on the standard error of prediction, range from 20 to about 80 percent (see section 4.4). The largest difference between the model results (which appears as a distinct outlier in fig. 13) occurs in the Massachusetts Bay watershed, where the SWAT estimate is about twice as large as the SPARROW yield.

5.1.3 Discussion of model comparisons

There are fundamental differences between the SPARROW and SWAT models in their descriptions of nitrogen sources and sinks, methods of parameter estimation, and spatial and temporal scales of measurement and prediction, which likely account for the

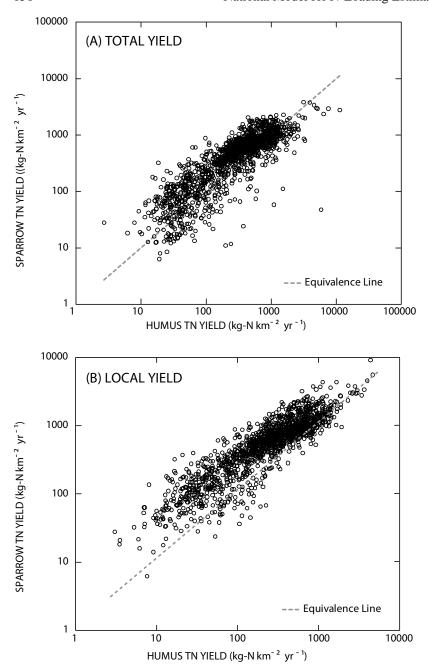


Figure 12. SPARROW and HUMUS model predictions of total nitrogen (TN) yield for 1,480 hydrologic cataloging units (HCU) in the central and eastern United States; (A) total yield for the entire drainage area above each HCU, inclusive of the nitrogen contributions of all upstream HCUs, (B) local yield reflecting the export from each HCU independent of inflows from upstream HCUs. Humus yields are adjusted to reflect atmospheric nitrogen as estimated by SPARROW.

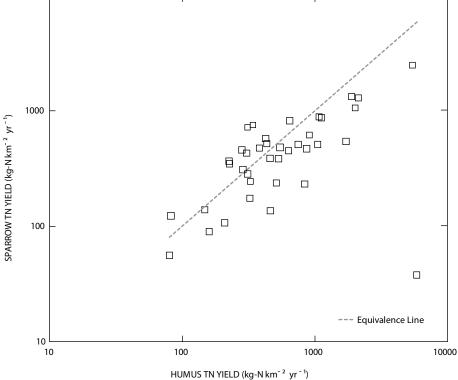


Figure 13. SPARROW and HUMUS model predictions of total nitrogen (TN) yield for major estuarine drainages of the United States. The yield reflects the total nitrogen export from the entire drainage area of each estuary.

observed differences in the model results. SWAT is a deterministic simulation model that uses field-scale experimental rates in combination with large-scale descriptions of watershed characteristics (e.g., soil, slope, crops) to quantify the supply, transformation, and delivery of nitrogen to streams and watershed outlets. By contrast, the rates of nitrogen supply and attenuation in SPARROW describe aggregate watershed-scale processes, and are quantified from a calibration of the model predictions to observed measurements of stream nitrogen flux. We highlight a few of the principle differences in the models to suggest some of the components that may contribute to the observed differences in predictions.

A prominent distinction between the models relates to descriptions of nitrogen inputs from agricultural sources. SPARROW relies on source input data (fertilizer use, livestock populations) for 1987 in combination with empirically derived rate coefficients to estimate the nitrogen supplied and delivered to streams. The model coefficients for agricultural inputs may represent the aggregate effect of multiple activities and watershed processes. By contrast, SWAT estimates agricultural inputs by applying a crop growth model that simulates nitrogen use by plants as a function of energy retention and biomass

conversion rates. This approach assumes that sufficient nitrogen is available to satisfy plant requirements. Crop harvest determines the quantities of residual nitrogen available for runoff. Thus, differences in the estimates of nitrogen availability between this method and SPARROW could partially explain the observed differences in estimates. Nitrogen from livestock wastes is also handled differently in the models. SPARROW estimates nitrogen inputs from livestock populations, whereas SWAT assumes that any nitrogen consumed by livestock is part of the residual crop nitrogen available for runoff.

The use of different time periods in describing average precipitation and streamflow conditions may account for some differences in model predictions. SWAT predictions are based on a long-term average of precipitation for a 30 year period, 1960-89, whereas SPARROW describes long-term mean hydrologic conditions for a base year 1987 using streamflow data covering a shorter time period, 1970-92. In view of evidence of modest increases in precipitation [Karl and Knight, 1998] and streamflow [Lins and Slack, 1999] in the conterminous United States during the past 30 years, mean conditions described by SPARROW could be slightly larger than those characterized by SWAT.

Differences in estimates of watershed attenuation were also noted among the models in comparisons of aquatic removal rates in the hydrologic units. Some of these differences may relate to differences in the spatial scale of model descriptions of stream channels. We found that the aquatic losses according to SPARROW are commonly larger and span a wider range than those reported by SWAT. The median percentage removed by SPARROW is about four times the percentage removed by SWAT (40% vs 10% of the nitrogen delivered to streams). SPARROW estimates of in-stream removal in the HCUs typically range from 20 to 70% of the nitrogen delivered to streams, whereas SWAT estimates commonly range from 5 to 14%. Because SPARROW yield estimates for the HCUs are generally larger than those of SWAT, it would appear that SPARROW estimates of the quantities of nitrogen delivered to streams are also larger than those estimated by SWAT.

5.2 Comparison with Chesapeake Bay Watershed Models

Two models of total nitrogen flux in the Chesapeake Bay watershed are available for comparison with regional estimates from the national SPARROW model, including the deterministic simulation model, HSPF, and a regionally calibrated SPARROW model. The Chesapeake Bay watershed is 164,000 square kilometers in size, 80 percent of which is drained by three rivers, the Susquehanna, Potomac, and James. The watershed contains areas predominantly in forest (60%), crop land (20%), urban land (10%), and pasture (9%) [Donigian *et al.* 1994].

5.2.1 Chesapeake Bay (CB) SPARROW model

The CB SPARROW model applies a similar statistical framework as was used in the national SPARROW model. More detailed descriptions of the model, its application, and

the input data sets can be found in Brakebill and Preston [1999] and Preston and Brakebill [1999]. As in the national model, the U.S. EPA River Reach File 1 (RF1) serves as the digital river network for the CB SPARROW model to which watershed attributes are spatially referenced. The model was refined by using a one-square kilometer digital elevation model (DEM) to define the watershed boundaries of each of the 1,400 reaches, thereby providing information for relating continuous spatial information on watershed characteristics to the stream network. Estimates of TN flux at 79 monitoring locations (see location map in fig. 14) were calculated from stream-discharge and TN concentrations according to methods described previously for the national SPARROW model. The drainage basin size for these monitoring stations ranges from 480 to 52,000 square kilometers. Eleven monitoring sites are common to the national SPARROW model.

Data on nutrient sources and watershed characteristics differed from those used in the national SPARROW model (but are primarily derived from those used in HSPF) with the exception of estimates of nitrate wet deposition and soil permeability. Nitrogen inputs from agricultural fertilizer and livestock wastes were quantified according to land-use data, county-level agricultural statistics, and documented nitrogen fertilizer application rates coupled with agricultural area [Gutierrez-Magness and others, 1997]. Point-source discharge information consisted of nitrogen-discharge measurements at specific locations throughout the watershed. Each point source was linked with a stream reach based on the stream network described above. Point-source loads were calculated from the average annual waste discharge for the period 1986-88. Urban area, determined from land-use data developed by EPA, NOAA and USGS, was included in the model as a possible source of nutrients.

The calibrated CB SPARROW model [Preston and Brakebill, 1999] consists of 10 explanatory variables[^] and explains approximately 96 percent of the variability in in-stream TN flux. The accuracy of the model predictions are similar to the national model;

the distribution of the percent absolute difference between the predicted and observed values has a median of 34 percent and an interquartile range from 18 to 61 percent. The explanatory variables and estimated coefficients for the TN model are presented in table 8. Estimates of uncertainty in the fitted coefficients in table 8 are expressed as 90 percent confidence intervals based on a bootstrap estimation procedure. Five source variables were found to be significant including municipal and industrial point sources, urban land, fertilizer use, livestock wastes, and atmospheric deposition. These source categories are similar to those in the national SPARROW model with the exception of the "urban land" class. The rates of in-stream total nitrogen removal are estimated according to three streamflow classes (a smaller flow class is defined in the CB SPARROW). The in-stream loss rates are Consistent with both the magnitude and the functional form (inverse relation to channel size) as those reported for the national model. The rates of in-stream nitrogen loss span approximately an order of magnitude from 0.07 day" in the largest rivers (> 28 m3/s) to 0.76 day⁻¹ in the smallest streams (< 5.7 m3/s). The loss rate for the smallest stream class (< 28.3 m3/s) in the national SPARROW model (0.45 day⁻¹) lies between the CB SPARROW loss rates (0.30 to 0.76 day⁻¹) estimated for streams of this size. In contrast to the national model, the CB SPARROW model has a separate loss rate for reservoirs.

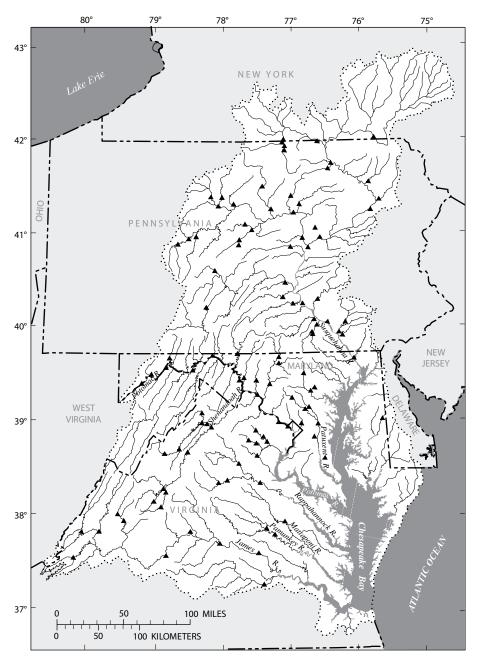


Figure 14. Locations of stream monitoring stations and RF1 reach segments in the Chesapeake Bay watershed. Station locations are denoted by a triangle.

TABLE 8. Chesapeake Bay SPARROW total nitrogen model coefficients based on a regression of stream nitrogen flux at 79 river monitoring stations on watershed characteristics.

| Model Parameters | Coefficient Units | Bootstrap Coefficient | Lower 90% CI ^a | Upper 90% CI ^a |
|--|--------------------------------------|--------------------------|------------------------------|---------------------------|
| Nitrogen source, $oldsymbol{eta}$ | | 4.50 | 0.555 | 2.40 |
| Point sources | dimensionless | 1.50 | 0.677 | 2.18 |
| Fertilizer application | dimensionless | 0.279 | 0.134 | 0.421 |
| Livestock waste production | dimensionless | 0.336 | 0.147 | 0.489 |
| Atmospheric deposition | dimensionless | 1.03 | 0.350 | 1.63 |
| Urban land | kg ha ⁻¹ yr ⁻¹ | 7.85 | 2.23 | 13.0 |
| Land-to-water loss coefficient, a Soil permeability In-stream loss rate, b, k | hr. cm-1 | 0.030 | -0.003 | 0.065 |
| $k_1 (Q < 5.8 \text{ m}^3 \text{ s}^{-1})$ | day ⁻¹ | 0.760 | 0.253 | 1.25 |
| k_2 (5.8 m ³ s ⁻¹ < Q <: 28.3 m ³ s ⁻¹) | day ⁻¹ | 0.302 | 0.092 | 0.507 |
| $k_3 (> 28.3 \text{ m}^3 \text{ s}^{-1})$ | day -1 | 0.067 | 0.000 | 0.162 |
| Reservoir loss rate | day -1 | 0.415 | 0.000 | 0.898 |
| R-Squared | | 0.961 | | |
| Mean square error | | 0.167 | | |
| Number of observations | | 79 | | |

^a Minimum bootstrap confidence intervals (CI).

5.2.2 HSPF model

The HSPF model provides a temporal and spatial description of nutrient loads from pervious and impervious land surfaces and transport through rivers and reservoirs [Bicknell *et al.* 1997]. The simulation of nutrient load depends on a nonpoint source component which includes applications of fertilizer, manure, atmospheric deposition, crop uptake, soil adsorption, and denitrification. This component simulates the transformations and improvement of various nitrogen species in the subsurface and surface runoff. The river and reservoir components include hydraulic behavior, sediment-nutrient interaction[^], nitrification, denitrification, and phytoplankton growth. The Chesapeake Bay watershed is segmented into 87 watershed sections that average 1,900 sq. kilometers in size [Shenk *et al.* 1998]. Regions of similar geographic and topological characteristics were I defined according to soil type, soil moisture capacity, infiltration rates, slope, and precipitation. A base year of 1985 was used for watershed characteristics, with hydrologic conditions averaged for the years 1985-94.

The hydrologic, land-use, soils, agricultural, and municipal and industrial point-source data used in the HSPF model are described in Shenk *et al.* [1998]. Atmospheric wet deposition data for nitrate and ammonia were obtained from 15 NADP monitoring sites in the region for 1984-91. Spatially continuous estimates of daily wet deposition to land and water surfaces of the watersheds were determined from a spatial regression of mean wet deposition at NADP sites on precipitation, latitude, and month of the year. Constant

b In-stream loss rates fit separately for stream reaches with mean streamflow (Q) corresponding to the indicated intervals.

concentrations were assigned to each model segment according to the regression. Spatial estimates of dry deposition were obtained from an application of a meteorological / chemical model, RADM [Regional Acid Deposition Model; Shenk *et al.* 1998; Gutierrez-Magness *et al.* 1997] in the eastern United States. These estimates are based on an estimated wet/dry ratio for each model cell of 400 sq. kilometers in the Chesapeake Bay region. The HSPF model was run both with and without the atmospheric deposition inputs to quantify the separate contributions of this source to total nitrogen exports in the watershed.

The CB HSPF was calibrated for 14 locations in the watershed based on the use of the observed measurements of concentration and flow. Ten of these locations were included among the 79 monitoring sites used in calibrating the CB SPARROW model. Based on the HSPF model predictions of the annual load at these 10 sites, the predicted TN yield is typically within 20 percent or less of the mean yield based on stream monitoring data (interquartile range = 14 to 30%).

5.2.3 Results and discussion of model comparisons

Figure 15 compares predictions of total nitrogen export from the national and CB SPARROW models and the HSPF model to "observations" of total nitrogen export at stream monitoring sites in the Chesapeake Bay watershed. The observed export is based on estimates of the mean annual load obtained by applying flux estimation techniques [Cohn *et al.* 1989] to stream monitoring records. SPARROW predictions are available for 79 monitoring locations; all of these sites were used in calibrating the CB SPARROW model and 11 were used in calibrating the national SPARROW model. HSPF predictions are compared to the mean annual load estimated from monitoring data at 25 of the sites;

the concentration and flow data from 10 of these sites were used in calibrating the HSPF model.

The comparisons indicate that the national SPARROW predictions of total yield are within at least 39 percent of the observed yield at one half of the sites; approximately one half of the predictions are within 19 to 82 percent of the observed yield (interquartile range). The magnitude of these differences between predicted and observed values are only slightly larger than previously described for the CB SPARROW model and for the national SPARROW calibration data. Differences between the observed values and HSPF model predictions are smaller than either of the SPARROW models; HSPF predictions are within at least 18 percent of the observed yield at one half of the sites;

about one half of the predictions are within 12 to 30 percent of the observed yield, hi Chesapeake Bay watersheds with yields less than 500 kg ha¹¹ yr¹ and flux less than $2x10^5$ kg yr", there is evidence that the national SPARROW model tends to over predict export (fig. 15). In these watersheds, the national SPARROW predictions typically exceed the observed yield by a factor of 2.2 (interquartile range of 1.6 to 2.9). Uncertainties in the national predictions for watersheds of this size are typically 40 to 80 percent, based on the standard error of prediction (see section 4.4). There is less evidence of bias in the national SPARROW predictions in watersheds with higher yields and flux. All of the models tend to slightly under predict in the highest yielding watersheds, above 3,000 kg

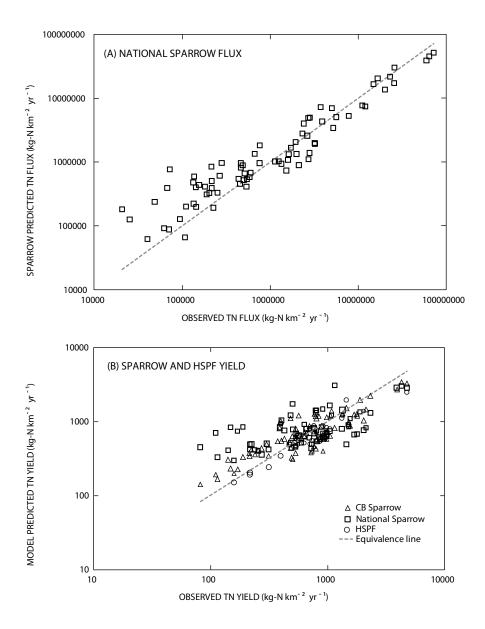


Figure 15. Model predictions of mean total nitrogen (TN) export from Chesapeake Bay (CB) watersheds in relation to the mean export observed at stream monitoring stations: (A) flux for the national SPARROW model; (B) yield for the CB and National SPARROW and HSPF models. The comparisons include 79 stream locations for the SPARROW model predictions and 26 locations for the HSPF model.

km⁻² yr⁻¹, where comparisons are available for SPARROW at three monitoring locations and for HSPF at one monitoring location.

In figure 16, we compared the various model predictions of atmospheric TN export for 46 locations in the Chesapeake Bay watershed common to the HSPF model segments and SPARROW reaches. The model predictions of atmospheric contributions (fig. 16b) show a positive correlation over the range of percentages. National SPARROW predictions are larger than HSPP predictions at most of the outlets of the interior watersheds. The national predictions are also larger than the CB SPARROW predictions at most of the watershed outlets although the interquartile ranges of the predictions overlap considerably (table 9). The national SPARROW predictions of the atmospheric contribution to stream export (table 9) typically range from 27 to 38 percent (interquartile range) with a median of 32 percent. By comparison, CB SPARROW predictions at the 46 interior watersheds typically range from 18 to 31 percent with a median of 24 percent. Both the HSPF and CB SPARROW model predictions are within the range of uncertainty (15 to 41 percent) in the national SPARROW predictions for the Chesapeake Bay watershed, based on the standard error in the mean atmospheric contribution of 28 percent (see section 4). Literature estimates of atmospheric contributions to the Chesapeake Bay from the surrounding watershed range from 24 to 59 percent [Valigura et al. 1996; Castro et al. this volume].

The observed differences in atmospheric contributions to stream TN flux are likely explained by differences in estimates of the inputs and supply of dry and wet nitrogen deposition as well as model estimates of terrestrial and aquatic attenuation of atmospheric nitrogen. In view of the similarities in estimates of wet nitrate deposition used in the SPARROW and HSPF models, differences in deposition inputs are more likely explained by other nitrogen forms (e.g., ammonium, organic wet deposition). For example, the mean national SPARROW estimate of wet nitrate deposition in the Chesapeake Bay watershed is 3.1 kg ha⁻¹ yr⁻¹. By comparison, the mean watershed estimate, based on wet nitrate deposition data used in HSPF, is 3.9 kg ha⁻¹ yr¹. Comparisons of the model estimates of in-stream nitrogen loss suggest that removal rates may be somewhat less in the national SPARROW model. This may partially explain the higher national SPARROW estimates of atmospheric and total nitrogen exports in the smaller watersheds. In-channel losses of TN average about 37 percent for streams in the Chesapeake Bay watershed according to the national SPARROW model (see section 4), whereas in-channel losses average from about 60 to 80 percent according to HSPF [Donigian et al. 1994] for the mean water travel time of Chesapeake Bay streams of about 5 days. Although the national SPARROW loss rate for small streams (mean flow < 28.3 m³ s⁻¹) is consistent with the rates estimated by the CB SPARROW (see section 5.2.1), larger quantities of nitrogen are removed in the smallest streams (mean flow < 5.8 m³ s⁻¹) according to the CB SPARROW.

6. Summary and Conclusions

An analysis of the contributions of the atmosphere to the nitrogen loads to major coastal and estuarine ecosystems in the United States was undertaken using an empirical

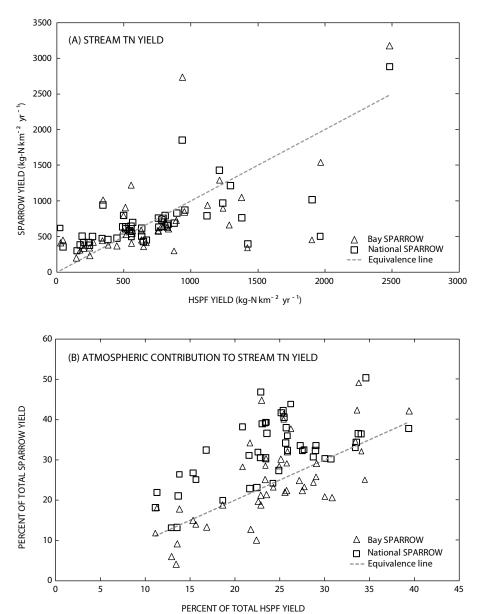


Figure 16. Model predictions for the National and Chesapeake Bay SPARROW and HSPF models for 46 interior drainage basins of the Chesapeake Bay: (A) mean total nitrogen (TN) yield; and (B) atmospheric contributions to mean total nitrogen yield.

TABLE 9. Predictions of the percentage contribution of atmospheric nitrogen sources to stream export at 46 locations in the Chesapeake Bay watershed.

| Model | | Atmospheric Contribution (percent) | | |
|---|------|------------------------------------|------|--|
| | 25th | Median | 75th | |
| National SPARROW | 27 | 32 | 38 | |
| Chesapeake Bay SPARROW | 18 | 24 | 31 | |
| HSPF (Hydrologic Simulation Program Fortran) Chesapeake Bay watershed model | 18 | 20 | 24 | |

[&]quot;The estimated mean atmospheric contribution for the entire Chesapeake Bay watershed is 28 percent with a standard error of prediction ranging from 15 to 41 percent (see results in section 4).

watershed model, SPARROW (Spatially Referenced Regression on Watershed attributes). In the 40 estuarine watersheds examined, the mean total nitrogen yield ranges from 38 to 2,500 kg km⁻² yr⁻¹. Atmospheric nitrogen contributions to riverine export range over nearly two orders of magnitude from 4 to 326 kg km⁻² yr⁻¹. The atmosphere is estimated to contribute from 4 to 35 percent of the total nitrogen in stream export with a median contribution of about 15 percent. The highest atmospheric contributions are observed in the northeastern and Mid-Atlantic watersheds of the United States (i.e., North Atlantic region). Uncertainties in the estimates, based on the standard error of prediction, range from 40 to 100 percent and vary inversely with watershed area. Among the 40 watersheds, agricultural sources contribute the largest shares of nitrogen, accounting for more than one third of the stream export in most of the watersheds (with contributions as large as 70 percent), followed by the aggregate contributions of other diffuse sources, including runoff and subsurface discharges from urban, forested, range, and barren lands. Municipal and industrial point sources are similar in magnitude to atmospheric contributions in most watersheds, but represent the largest share (35-88%) of nitrogen in one half of the North Atlantic watersheds and in several Gulf region watersheds. Comparisons of the SPARROW model with other national and regional watershed models indicate general agreement in the predictions of TN export over a wide range of watershed sizes, but illustrate the intrinsic difficulties of comparing the flux rates of models having different temporal and spatial scales of measurement and prediction and different specifications of nitrogen supply, transformation, and transport processes.

Improvements in our knowledge of the relative contributions of nitrogen sources to coastal waters provides an important initial step in developing strategies for controlling nitrogen enrichment of coastal ecosystems. However, information that describes the watersheds and source locations responsible for coastal nitrogen inputs, as illustrated in the analysis for the Chesapeake Bay, is also needed to assist in the design of efficient management strategies. The current analysis provides an empirical framework for using stream monitoring records and data on watershed characteristics to identify the

geography of nitrogen sources to coastal ecosystems and to refine model assumptions regarding the processes governing nitrogen transport through watersheds. Use of more spatially-detailed land-cover and hydrologic data and stream measurements from small watersheds are likely to enable a better separation of nitrogen sources and small-channel and terrestrial loss processes. Moreover, the addition of model functions and data to explicitly account for the effects of subsurface transport, specific agricultural practices, and seasonal and interannual variations, may provide more accurate prediction of the origins of nitrogen delivered to coastal waters. These assessments are likely to benefit from a continued effort| to integrate the mechanistic descriptions of deterministic models with the empirical methods of estimating watershed-scale rate processes and their uncertainties in statistical models.

Acknowledgments

The authors would like to thank Keith Robinson, Gary Shenk, Suzanne Bricker, and Bruce Hicks for comments on earlier versions of the chapter. Thanks to Michael lerardi for assistance in preparing the graphics.

References

- Alexander, R.B., Brakebill, J.W., Brew, R.E., and Smith, R.A., ERF1—Enhanced River Reach File 1.2, U.S. Geological Survey Open-File Report 99-457, Reston, Virginia (1999). Alexander,
- R.B., Slack, J.R., Ludtke, A.S., Fitzgerald, K.K. & Schertz, T.L., Data from selected U.S. Geological Survey national stream water quality monitoring networks, *Wat. Resour. Res.* 34, 2401-2405 (1998).
- Alexander, R.B. and Smith, R.A., County level estimates of nitrogen and phosphorus fertilizer use in the United States, 1945 to 1985, *U.S. Geological Survey Open-File Report 90-130*, Reston, Virginia (1990).
- Alexander, R.B., Smith, R.A., and Schwarz, G.E., Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico, *Nature* 403, 758-761 (2000).
- Arnold, J.G., R. Srinivasan, R.S. Muttiah and R.H. Griggs, Watershed Modeling and GIS with SWAT and GRASS. SWAT User's Manual. Blackland Research Center, TexasAgricultural Experiment Station, Temple, Texas (1995).
- Arnold, J.G., Williams; J.R., & Maidment, D.R., A continuous-time watershed sediment routing model for large basins, *ASCEJ. Hydr. Eng. 121*, 171-183 (1995).
- Arnold, J.G., Williams, J.R., Nicks, A.D., & Sammons, N.B., SWRRBWQ A basin scale simulation model for soil and water resources management, Texas A&M University Press, College Station, Texas, USA (1990).
- Battaglin, W.A. & Goolsby, D.A., Spatial data in geographic information system format on agricultural chemical use, land use, and cropping practices in the United States, U.S. Geological Survey Water Resources Investigations Report 94-4176 (1994).
- Beaulac, M.N. & Reckhow, K.H., An examination of land use nutrient export relationships, Wat. Res. Bull. 18, !!013-1024 (1982). 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).
- Bicknell, B.R., Imhoff, J.C., Kittle, J.L., Jr., Donigian, A.S., Jr., & Johanson, R.C., Hydrological simulation program - fortran user's manual for release 11, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, USA, EPA/600/R-97/080, 755 p. (1997).
- Brakebill, J.W. and Preston, S.D., Digital data used to relate nutrient inputs to water quality in the Chesapeake Bay watershed. Version 1.0: *U.S. Geological Survey Open-File Report99-6*, Baltimore, Maryland (1999) at URL http://md.usgs.gov/publications/ofr-99-60/.
- Castro, M.S., Driscoll, C., Jordan, T.E., Reay, W., Seitzinger, S., Stiles, R., & Cable, J., Assessment of the contribution made by atmospheric nitrogen deposition to the total nitrogen load to thirty-four estuaries on the Atlantic and Gulf coasts of the United States, this volume.
- Cohn, T.A., DeLong, L.L., Gilroy, E.J., Hirsch, R.M. & Wells, D.K., Estimating constituent loads, Wat. Resour. Res. 25, 937-942 (1989). Council on Environmental Quality (CEQ), Environmental trends. Executive Office of the President, Washington, D.C. 64-65 (1989).
- Delwiche, L.L., & Haith, D.A., Loading functions for predicting nutrient losses from complex watersheds, *Water Resour. Bul. 19*, 951-959 (1983).
- DeWald, T., Horn, R., Greenspun, R., Taylor, P., Manning, L., & Montalbano, A., STORET reach retrieval documentation, U.S. Environmental Protection Agency, Washington, D.C. (1985).
- Diaz, R.J. & Rosenberg, R., Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna, *Oceanog. Marine Biology: an Annual Review 33*, 245-303 (1995).
- Donigian, A.S., Jr., Bicknell, B.R., Patwardhan A.S., Linker, L.C., & Cliang, C.H., Watershed model application to calculate bay nutrient loadings: Final findings and recommendations, U.S. Environmental Protection Agency, Chesapeake Bay Program Office, Annapolis, Maryland, USA (1994).
- Efron, B., The jackknife, the bootstrap and other resampling plans, in CBMS-NSF Regional Conference Series in Applied Mathematics, Soc. For Ind. And Appl. Math., Philadelphia, Pa., USA (1982).
- ESRI (Environmental Systems Research Institute, Inc.), ARC/INFO user's guide: Surface modeling with TIN. Version 7.0, 1996.
- Fisher, D.C. & Oppenheimer, M., Atmospheric nitrogen deposition and the Chesapeake Bay estuary, *Ambio.* 20,102-108 (1991).
- Frink, C.R., Estimating nutrient exports to estuaries, J. Environ. Qual. 20,717-724 (1991).
- Gilroy, E.J., Hirsch, R.M., & Cohn, T.A., Mean square error of regression-based constituent transport estimates, Water Resour. Res. 26, 2069-2077 (1990).
- Gutierrez-Magness, A.L., Hannawald, J.E., & Linker, L.C., Appendix E: Phase IV watershed land uses and model linkages to the airshed and estuarine model, in Chesapeake Bay Watershed Model Application and Calculation of Nutrient and Sediment Loadings, EPA 903-R-97-019, U.S. Environmental Protection Agency, Chesapeake Bay program office, Annapolis, Maryland, USA, 142 p. (1997).
- Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch & Zhu Zhao-liang, Regional nitrogen budgets and riverine N & P fluxes for the drainages to

- the North Atlantic Ocean: natural and human influences, *Biogeochem. 35*, 75-139 (1996).
- Jaworski, N.A., Groffnan, P.M., Keller, A.A. & Prager, J.C., A watershed nitrogen and phosphorus balance: the Upper Potomac River basin, Estuaries 15, 83-95 (1992).
- Jaworski, N.A., Howarth, R.W. & Hetling, L.J., Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast United States, *Environ. Sci. Techno.* 31, 1995-2004(1997).
- Johnes, P.J. Evaluation *find* management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach, *J. of Hydrology 183*, 323-349 (1996)
- Johnes, P.J. & Heathwaite, A.L., Modelling the impact of land use change on water quality in agricultural catchrrtents, *Hydrological Processes* 11, 269-286 (1997).
- Johnson, D.W., Nitrogen retention in forest soils, J. Emir. Qual. 21,1-12 (1992).
- Jordan, T.E. & Weller D.E., Human contributions to terrestrial nitrogen flux: assessing the sources and fates of anthropogenic fixed nitrogen, *Bioscience* 46, 655-664 (1996).
- Karl, T.R., & Knight, R.W., Secular trends of precipitation amount, frequency, and intensity in the United States, *Bulletin of the American Meteorological Society* 79, 231-241 (1998).
- Lins, H.F., & Slack, J.R., Streamflow trends in the United States, Geophysical Research Letters 26, 227-230 (1999).
- Meyers, T., Sickles, J., Dennis, R., Russell, K., Galloway, J., & Church T., Atmospheric nitrogen deposition to coastal estuaries and their watersheds, this volume.
- Mueller, D.K., Ruddy, B.C. & Battaglin, W.A., Logistic model of nitrate in streams of the upper-midwestem United States, *J. Environ. Qual.* 26, 1223-1230 (1997).
- Muttiah R.S., R. Sriniyasan, and P.M. Alien, Prediction of two-year peak stream discharges using neural networks. *J. Am. Water Res. Assoc.* 33, 625-630 (1997).
- National Agricultural | Statistics Service (NASS), Historic data on livestock, Economic Statistics System, Washington, D.C., on-line database (1998).
- National Atmospheric reposition Program, NADP/NTN Annual data summary: Precipitation chemistry in the United States, Nat. Resour. Ecol. Lab., Colorado State Univ., Fort Collins, CO, 1983 to 1993.
- Nixon, S.W., Coastal marine eutrophication: a definition, social causes, and future concerns, *Ophelia 41*, 199-219(1995).
- Novotny, V., and H. Ulem, Water quality: Prevention, identification, and management of diffuse pollution. Van Nostrand Reinhold, New York (1994).
- Peierls, B.L., Caraco,!N.F., Pace, M.L. & Cole, J.J., Human influence on river nitrogen, *Nature 350*, 386-387 (1991).
- Preston, S.D. and Brakebill, J.W., 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).
- Rastetter, E.B., King, A.W., Cosby, B.J., Hornberger, G.M., O'Neill, R.V., & Hobbie, J.E., Aggregating fine-scale ecological knowledge to model coarser-scale attributes of ecosystems, *Ecological Apps.* 2, 55-70 (1992).
- Ritter, W.F., Reducting impacts of nonpoint source pollution from agriculture: a review, *J. Environ. Sci. Health* 23, 645-667 (1988).
- Rutherford, J.C., Williamson, R.B., & Cooper, A.B., *Nitrogen, phosphorus, and oxygen dynamics in rivers. In* Inland Waters of New Zealand (ed.) A.B. Viner, 139-165 (1987).

- SAS Institute, Inc., SAS/ETS user's guide. Version 6, 2nd edition, Cary, North Carolina, USA, 509-591 (1993).
- Seitzinger, S.P. & C. Kroeze, Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems, *Global Biogeochem. Cycles* 12, 93-113 (1998).
- Seitzinger, S.P., Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance, *Limnol. Oceanogr.* 33, 702-724 (1988).
- Shenk, G.W., Linker, L.C., & Donigian, A.S., The Chesapeake Bay program models, Proceedings of the First Federal Interagency Hydrologic Modeling Conference, Las Vegas, Nevada, USA, U.S. Environmental Protection Agency, Chesapeake Bay Program Office, Annapolis, Maryland, USA, 8 p. (1998).
- Smith, R.A., G.E. Schwarz & R.B. Alexander, Regional interpretation of water-quality monitoring data, *Wat. Resour. Res. 33*, 2781-2798 (1997).
- Srinivasan, R., Arnold, J.G., Muttiah, R.S., Walker, D., & Dyke, P.T., Hydrologic unit modeling of the United States (HUMUS), In'. Advances in hydro-science and engineering, S. Yang (ed.) Vol I, Part A., 451-456, Washington, D.C., USA (1993).
- Tasker G.D., and N.E. Driver, Nationwide regression models for predicting urban runoff water quality at unmonitored sites. *Water Resources Bulletin* 24,1091-1101 (1988).
- Thomann, Systems analysis and water quality management. Environmental Research and Applications, Inc., New York, N.Y. (1972).
- United States Environmental Protection Agency, Design manual: Onsite wastewater treatment and disposal systems, Office of Water Programs Operations, Washington, D.C., EPA 625/1-80-012 (1980).
- Valigura, R.A., Luke, W.T., Artz, R.S., & Hicks, B.B., Atmospheric nutrient input to coastal areas: reducing the uncertainties, *NOAA Coastal Ocean Program Decision Analysis Series No. 9*, 24 p. (1996).
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H. & Tilman, D.G., Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 7, 737-750 (1997).
- Whitehead, P.G., Wilson, E.J., & Butterfield, D., A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchments (INCA): Part I model structure and process equations, *Sci. of the Total Environ.* 210/211, 547-558 (1998).
- Williams, J.R., Nicks, A.D., & Arnold, J.G., Simulator for water resources in rural basins, *ASCEJ. Hydr. Engr. Ill*, 970-986 (1985).