Natural Background Concentrations of Nutrients in Streams and Rivers of the Conterminous United States

Richard A. Smith, Richard B. Alexander, and Gregory E. Schwarz

Environ. Sci. Technol., **2003**, 37 (14), 3039-3047• DOI: 10.1021/es020663b • Publication Date (Web): 13 June 2003

Natural Background Concentrations of Nutrients in Streams and Rivers of the Conterminous United States

RICHARD A. SMITH,*
RICHARD B. ALEXANDER, AND
GREGORY E. SCHWARZ

U.S. Geological Survey, Reston, Virginia 20192

Determining natural background concentrations of nutrients in watersheds in the developed world has been hampered by a lack of pristine sampling sites covering a range of climatic conditions and basin sizes. Using data from 63 minimally impacted U.S. Geological Survey reference basins, we developed empirical models of the background yield of total nitrogen (TN) and total phosphorus (TP) from small watersheds as functions of annual runoff, basin size, atmospheric nitrogen deposition rate, and region-specific factors. We applied previously estimated in-stream loss rates to yields from the small watershed models to obtain estimates of background TN and TP yield and concentration throughout the stream/river network in 14 ecoregions of the conterminous United States. Background TN concentration varies from less than 0.02 mg L^{-1} in the xeric west to more than 0.5 mg L^{-1} along the southeastern coastal plain. Background TP concentration varies from less than 0.006 mg L^{-1} in the xeric west to more than 0.08 mg L^{-1} in the great plains. TN concentrations in U.S. streams and rivers currently exceed natural background levels by a much larger factor (6.4) than do TP concentrations (2.0). Because of local variation in runoff and other factors, the range of background nutrient concentrations is very large within some nutrient ecoregions. It is likely that background concentrations in some streams in these regions exceed proposed nutrient criteria.

Introduction

Over the past four decades, scientific interest in determining natural water quality has increased markedly because of the greatly increased potential for human influence on water quality that has accompanied economic and technological development (*1*, *2*). Natural background conditions for aquatic nitrogen and phosphorus are currently of particular interest and importance because cultural sources of biologically active forms of those elements have increased dramatically in many aquatic environments (*2*, *3*). Increases in aquatic nutrients can be traced to population growth as well as per capita increases in synthetic fertilizer production and use, fossil fuel combustion, meat consumption, and export of agricultural products (*2*, *3*). Because of infrequent monitoring of water quality prior to the first decade of the twentieth century (*4*), nutrient levels in surface waters during the period of European settlement of North America have been largely a matter of conjecture. Data from reference sites, however, provide a potential baseline for estimating the extent of change in nutrient levels in developed watersheds that has occurred since the time that cultural sources of nitrogen and phosphorus first began to affect aquatic ecosystems.

Federal, state, and tribal officials in the United States are currently attempting to develop preliminary criteria and standards for total nitrogen (TN) and total phosphorus (TP) in the nation's surface waters to reduce the risk of eutrophication (*5*−*7*). To allow for regional variation in nutrient criteria, the U.S. Environmental Protection Agency (EPA) has divided the nation into 14 "nutrient ecoregions" (*5*) based on climate, physiography, and vegetation cover (Figure 1). Although the goal of criteria development is not to set nutrient standards at natural background levels, knowledge of the range of background levels in each region would serve as a useful frame of reference. Specifically, the EPA recommends that state and tribal governments use the 75th percentile values from regional distributions of background nutrient concentrations as the lower end of the appropriate range for choosing state criteria. Data from long-term reference sites in these regions provide a potential source of information for developing regional background concentration distributions.

However, there are three major obstacles to using nutrient data from reference sites in this country and other industrialized nations to define natural background conditions:

(i) Pristine reference sites are essentially nonexistent in most regions of the industrialized world because of extensive land use and the ubiquitous presence of anthropogenic fixed nitrogen in atmospheric deposition (*8*). Indeed, many state governments in the United States establish reference sites in moderately developed watersheds in order to provide a practical baseline for comparison with more intensively developed basins (*9*). For this reason, it is necessary to distinguish between *natural background conditions* and the more general term *background* (or *reference*) *conditions* when describing the water quality conditions at reference sites. Moreover, any method for using reference site data from developed regions to determine natural background conditions for aquatic nutrients must include some means of correcting for cultural sources, especially atmospheric nitrogen.

(ii) Nutrient yields at undeveloped reference sites vary by more than 2 orders of magnitude (*8*, *10*, *11*) because of variations in any of several basin characteristics including climate, hydrology, natural vegetation (*8*), and the mineral composition of soil and rock (*12*). Thus, estimates of background conditions for developed regions should reflect the natural characteristics of the specific watersheds of interest.

(iii) Nearly all reference sites in the United States and other industrialized countries are located in small watersheds because few large watersheds remain undeveloped in these areas. Thus, little is actually known about background nutrient levels in large rivers in the developed world due to the difficulty of "scaling up" the results obtained from small reference watersheds (*13*, *14*). In general, nutrient yields and concentrations would be expected to decline with increasing basin size due to loss processes that reduce nutrient mass as it travels downstream through stream channels. Moreover, the rate of in-stream loss has been shown to vary with channel size (*15*, *16*), further complicating the problem. To date, no method of adjusting for the effect of in-stream losses has

* Corresponding author phone: (703)648-6870; fax: (703)648-6693; e-mail: rsmith1@usgs.gov.

10.1021/es020663b
Published on Web 06/13/2003

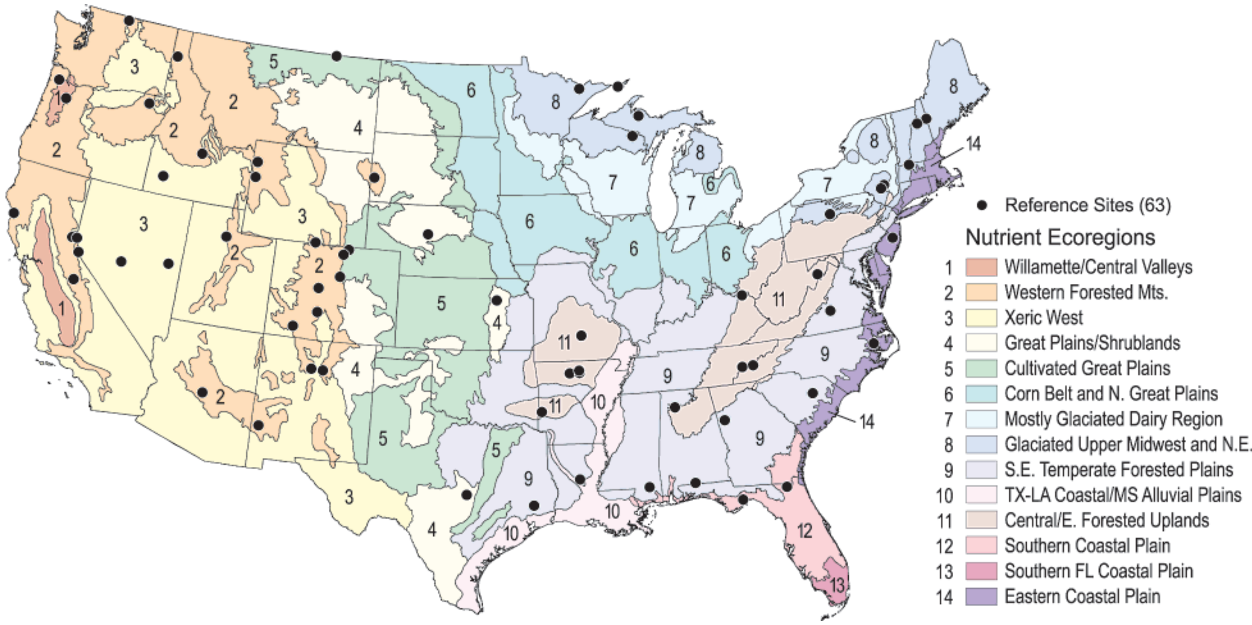

FIGURE 1. Nutrient ecoregions of the conterminous United States and the location of USGS reference sites used in this study (see ref *10* and Table S1 in the Supporting Information).

been applied to data from small reference streams to estimate background nutrient conditions in larger rivers.

Past analyses of reference site data have identified annual runoff as a strong predictor of background nutrient yields. Using data from 17 watersheds with minimal anthropogenic sources of nitrogen in the American tropics and the Gambia River basin (Africa), Lewis et al. (*8*) found that the mean annual yield of total fixed nitrogen (TN) and its component species are strongly correlated with mean annual runoff (stream flow per unit drainage area) in log−log models. Mean runoff logically is a strong predictor of TN yield because it is related to the density and composition of basin vegetation and is the primary mobilizing force for stored nitrogen (*8*, *17*). More recent analysis (*18*) of data from 20 stations in the U.S. Geological Survey (USGS) Benchmark Network also resulted in a regression model for log TN yield as a function of log runoff. Atmospheric deposition was not a significant predictor of TN, although it was a significant predictor of nitrate, ammonium, and dissolved organic N. It is possible that the range of conditions included in the 20 station data set was not adequate to show the effects of atmospheric deposition on TN (*18*). In fashion similar to the recent studies of TN, Gilliom (*19*) found that annual total phosphorus (TP) yield varied as a function of log(runoff) in 25 forest streams in the Puget Sound region where mean runoff rates for the streams varied over more than an order of magnitude. Together, these studies suggest that some of the variation in background nutrient yields observed over a wide latitudinal and climatic range can be accounted for with simple functions of mean runoff. However, such models are of limited practical value in predicting background nutrient levels for rivers and streams in developed regions because they do not account for (i) the effects of atmospheric deposition or other local characteristics or (ii) loss processes operating on nutrients as they are transported downstream to larger channels.

The purpose of this study is to develop models that overcome the above limitations and to use them to estimate regional frequency distributions for mean annual background TN and TP yield and concentration in streams and rivers of the conterminous United States. We emphasize the estimation of regional percentile statistics (specifically quartile values) in this study rather than single-point estimates of yield and concentration and, thus, take advantage of the generally smaller prediction error of the former in statistical models. Moreover, the current EPA policy for developing water quality criteria for nutrients is based on the quartiles of concentration distributions.

Our approach consists of three steps: First, we calibrate regression models for total nitrogen and total phosphorus yields in 63 minimally developed headwater streams (*10*) as functions of runoff, drainage area (TP), atmospheric deposition (TN), and region-specific factors. Second, we use these models to estimate background nutrient loadings from headwater streams to individual reaches in the RF1 stream/river network (*20*) of the conterminous United States. Finally, we use in-stream TN and TP loss rates from previously calibrated large watershed models to estimate downstream transport of background nutrient loads throughout the stream/river network. The resulting predictions of yields and concentrations are mapped and summarized as region-specific frequency distributions.

Methods

Regression Models. The principal goal of the regression analysis is the derivation of models predicting background yields of TN and TP in headwater streams (defined here as first-order or smaller within the RF1 stream network). Ideally, such models would predict nutrient yield from data on natural and atmospheric nutrient sources as well as factors that mediate the transport of nutrients to streams. Because the reference watersheds available for analysis have not received quantitative soil and vegetation surveys, information related to nutrient sources and transport at the sites is limited to (a) runoff, (b) basin area, (c) atmospheric nitrogen deposition rate, and (d) qualitative characteristics of the nutrient ecoregion containing the site (*21*). Runoff is included in the models because of its relation to the density and composition of natural vegetation as well as to transport efficiency (*8*). Basin area has been shown to influence nutrient yield under some land cover conditions (*22*). Ecoregional effects are included in the models as indicator (i.e., discrete) variables intended to account for unquantified regional characteristics such as physiography, soil type, and vegetation type, which potentially affect both the sources of nutrients and the efficiency of their export from the reference basins (*21*). Their inclusion as indicator variables also provides a statistical basis for testing the importance of ecoregional location to background nutrient yield independent of the effects of runoff and atmospheric deposition (see Regional Indicator Variables in the Supporting Information).

Regressions of TN yield on watershed characteristics were conducted using models of the form:

$$\ln Y_j = \ln\lfloor(\mathbf{b}_R \mathbf{R}_j Q_j^{b_{Q(\mathrm{source})}} + b_D D_j) Q_j^{b_{Q(\mathrm{delivery})}} A_j^{b_A}\rfloor + \epsilon_j \quad (1)$$

where Y_j is the nutrient yield (kg km^{-2} yr^{-1}) from basin j, Q_j is the runoff in basin j (cm yr^{-1}), A_j is the area of basin j (km^2), D_j is the atmospheric deposition in basin j (kg km^{-2} yr^{-1}); $b_{Q(\mathrm{source})}$, $b_{Q(\mathrm{delivery})}$, b_A , and b_D are the estimated parameters for the effects of runoff as a source, runoff as a delivery factor, basin area, and atmospheric deposition, respectively; $\mathbf{R}_j$ is a vector of regional indicator (discrete) variables with associated coefficients represented by the row vector $\mathbf{b}_R$; and ϵ_j is the model error, assumed to be independent and identically distributed across basins. Equation 1 is an elaboration of the model used by Lewis et al. (*8*) and Lewis (*18*) in previous analyses of background nitrogen yield as a function of runoff. Factors associated with sources of nitrogen are located within the parentheses of eq 1, and factors affecting the delivery of nitrogen mass from sources to the basin outlet appear outside the parentheses. Note that runoff appears in the equation for TN twice, once as a proxy for basin vegetation (mediated by a region-specific multiplicative coefficient) and a second time as a factor affecting nitrogen delivery from natural and atmospheric sources. The model for TP regressions was a reduced form of eq 1 based on the assumption that atmospheric deposition of phosphorus is a very minor contributor to TP in the reference basins for this study and is adequately dealt with through the regional coefficients, $\mathbf{b}_R$. In the reduced form of eq 1, runoff appears only once along with a single estimated parameter (b_Q) that combines the source and delivery effects of flow. Development of the regional indicator variables is described in the Supporting Information.

Integration of Nutrient Yield Models with SPARROW Transport Model. The TN and TP yield models developed above describe background nutrient yields in headwater stream basins (median basin area of reference sites used here = 150 km^2). To account for losses occurring during transport in larger streams and rivers, the TN and TP yield models were used to quantify the nutrient sources in a SPARROW (Spatially Referenced Regression on Watersheds) model of nonconservative transport in the RF1 national stream and river network (see Data Sources). The development and structure of the SPARROW model are described by Smith et al. (*23*). More recent estimates of TN channel loss rates (those used here) are given in Alexander et al. (*16*). Losses occurring during transport in stream channels and reservoirs are expressed as first-order functions of reach length, water velocity, and stream flow. First-order rate coefficients were estimated in nonlinear (SPARROW) regressions of TN and TP monitoring records from 374 and 381 sites, respectively (*16*, *23*) (see Table S2 in the Supporting Information). Use of these coefficients in this study requires the assumption that background nutrient conditions would not substantially alter the effective first-order coefficient values.

The nutrient load delivered to each RF1 reach was assumed to equal the contributing drainage area of the reach times the predicted background yield in the reach drainage based on runoff, regional location, atmospheric nitrogen deposition rate, and drainage area (TP only; see below). Combining the background yield and in-stream loss expressions gives the following equation for background nutrient transport through the RF1 network:

$$L_i = \sum_{j \in J(i)} Y_j A_j [\exp(-\mathbf{k}'\mathbf{T}_{i,j})] \quad (2)$$

where L_i is the nutrient transport (kg yr^{-1}) in reach i, Y_j is the nutrient yield in the drainage to reach j (from eq 1), $J(i)$ is the set of all reaches upstream of reach i, A_j is the contributing drainage area of reach j, $\mathbf{T}_{i,j}$ is a vector of channel attributes that mediate in-stream (and in-reservoir) loss between reach j and reach i, and $\mathbf{k}$ is a vector of estimated first-order coefficients applied to the attributes contained in $\mathbf{T}_{i,j}$. To simulate natural transport rates in the current application, reservoir loss coefficients were replaced with the channel loss coefficients applicable to the river reaches flowing through the reservoirs ($\mathbf{k}$ in eq 2; see Supporting Information).

The corresponding equation for flow-weighted concentration is obtained by dividing load by flow:

$$C_i \equiv \frac{L_i}{Q_i} = \frac{\sum_{j \in J(i)} Y_j A_j [\exp(-\mathbf{k}'\mathbf{T}_{i,j})]}{Q_i} \quad (3)$$

where C_i is the concentration in reach i, and Q_i is the stream flow in reach i.

All predictions from the background yield and concentration models are corrected for logarithmic re-transformation bias using the bootstrap method described in Smith et al. (*23*) with an additional constraint against negative values of the in-channel loss coefficients (*16*). The procedure typically resulted in a 15−20% bias correction.

Data Sources. Stream nutrient data were obtained from a database developed in a study of USGS reference sites by Clark et al. (*10*) (See Table S1 in the Supporting Information). The database includes nutrient records for a total of 82 sites operated by the USGS Benchmark (HBN), National Water Quality Assessment (NAWQA), and National Research Programs for the period 1976−1997. Mean annual TN and TP yield estimates in the database were based on the estimator method (*24*) and are available for a total of 63 HBN and NAWQA sites. Estimator model calibration was based on concentration and flow records for 1976−1997, while mean yield estimates (model application) were based on continuously gauged discharge divided by basin area for the 1990−1995 period (*10*). Runoff estimates at the hydrologic unit level were based on the study by Gebert et al. (*25*). Estimates of mean annual wet atmospheric deposition of TN for the sites were developed for this study from National Atmospheric Deposition Program (NADP) records from the early 1980s through 1993 (see Supporting Information). A GIS coverage of the boundaries of the National Nutrient Ecoregions (*21*) was used to determine the regional location of the reference sites (Figure 1). For four reference sites located very near regional boundaries, regional location was determined on the basis of annual precipitation and site descriptions given in Cobb and Biesecker (*26*).

River reaches for the conterminous United States were defined according to the U.S. EPA River Reach File (RF1) (*20*), consisting of 60 221 reaches. The drainage areas for reaches were obtained from 1-km digital elevation model data for North America (*27*).

Results and Discussion

Calibration of Background Yield Models. The results of the yield model calibrations are presented in Table 1. The R^2 values for TN and TP are 0.81 and 0.73, respectively, and standard errors for TN and TP are 72% and 65%, respectively. Basin area was not a statistically significant predictor of TN (p = 0.97) and was excluded from the final TN model. Atmospheric deposition of TP was assumed to be negligible and was excluded from the TP model. The statistically

TABLE 1. Model Parameters for Regressions of Nutrient Yield on Basin Characteristics for 63 USGS Reference Sites[a]

model component	parameter	standard error	*T* statistic	*P* value
Total Nitrogen				
regional indicator var. 1 (b_1)	1.604	0.963	1.67	0.1013
regional indicator var. 2 (b_2)	4.941	2.924	1.69	0.0965
regional indicator var. 3 (b_3)	0.484	0.538	0.90	0.3727
runoff, as source ($b_{Q\ source}$)	0.485	0.291	1.67	0.1007
runoff, as delivery factor ($b_{Q\ delivery}$)	0.551	0.181	3.04	0.0036
atmospheric deposition (b_D)	0.015	0.009	1.67	0.1001
R^2	0.810			
standard error (%)	72			
Total Phosphorus				
regional indicator var. 1 (b_1)	0.233	0.091	2.55	0.0133
regional indicator var. 2 (b_2)	0.535	0.207	2.58	0.0124
regional indicator var. 3 (b_3)	0.150	0.062	2.43	0.0183
runoff (b_Q)	0.807	0.064	12.61	0.0001
drainage area (b_A)	0.142	0.053	2.68	0.0095
R^2	0.733			
standard error (%)	65			

[a] See eq 1.

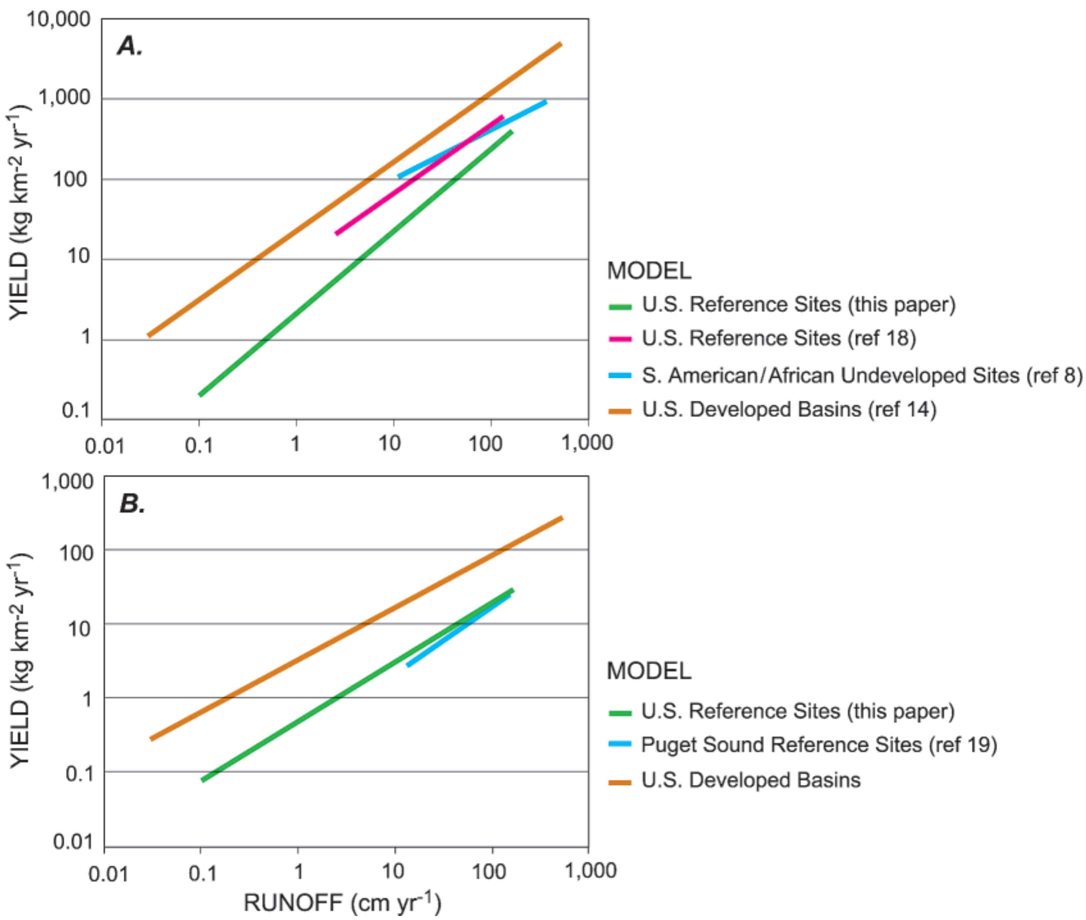

FIGURE 2. Previously published models of nutrient yield as a function of mean runoff as compared with models developed here: (A) deposition-corrected total nitrogen (TN); (B) total phosphorus (TP). The range of mean runoff shown for each line corresponds to that observed in each study. TN results shown for this study are based on the mean value of the regional indicator coefficients. TP results shown for this study are based on mean basin area and the mean value of the regional indicator coefficients.

strongest explanatory variable in both the TN and TP models (Table 1) is runoff, a result that is consistent with previous efforts to explain geographic differences in background nutrient yields (*18*). The inclusion of explanatory variables other than runoff (i.e., basin size, atmospheric deposition, and region indicator variables) in the TN and TP yield models increased the R^2 values by 16% and 30%, respectively, and lowered standard errors by 22% and 29%, respectively, as compared to regressions on runoff alone. (See Supporting Information for plots of predicted versus observed data.)

Figure 2 compares the relationship between mean TN yield and runoff observed in this study with that observed by Lewis et al. (*8*) for undisturbed watersheds in the tropical Americas and Africa and a more recent study by Lewis (*18*) for a subset of USGS Benchmark watersheds in the United States. The latter work was based on 20 of the watersheds used in the present study but tracked TN and other nitrogen species only during 1981−1982 and did not correct for atmospheric deposition. Mean TN yield for the 20 stations and 2-yr sampling period averaged more than three times the mean TN yield for the 63 stations included here for the period 1976−1997, thus explaining the higher line in Figure 2 for the Lewis study. A fourth line in Figure 2 depicts a recent (*14*) regression of TN yield on runoff for 691 developed watersheds in the United States. Predicted TN yields in the developed basins range from 4 to 10 times the deposition-corrected background TN yields over the observed range in runoff rates. Howarth et al. (*13*) reported a similar range in the effects of development on TN yield. The unpolluted tropical yields (*8*) exceed the deposition-corrected background TN yields for the present study by a factor of from 1.5 to 5 depending on runoff [Figure 2; see also Downing et al. (*28*)]. Note that all slopes in the log−log relationships between TN yield and runoff (Figure 2) for the temperate United States are statistically higher than for the tropical study, a reflection of very low TN yields from the extremely arid basins included in the temperate data.

The TP yield model developed in this study is compared in Figure 2 to one based on data from Gilliom (*19*) for 24 forested reference sites in the Puget Sound region. The two models are very similar for runoff rates from 12 to 150 cm yr^{-1}, the range observed in the Puget Sound study. The runoff slopes of the model developed here and of the Puget Sound model are 0.81 and 0.90, respectively, and are not statistically distinguishable. A regression of TP yield on runoff for 180 developed watersheds in the United States, however, has a runoff slope of 0.71, which is statistically distinguishable from the slopes of both reference site models. A somewhat lower runoff slope might be expected for TP in developed watersheds due to the contribution of point-source phosphorus (for which the runoff slope would approach zero).

Transport of Nutrients through the Stream/River Network. The results of combining the background yield models with the SPARROW transport model (eq 2) are summarized by nutrient region in Figure 3. Results of applying the corresponding concentration model (eq 3) are presented in Figure 4 (see also Figure 7). The box plots in Figures 3 and 4 summarize the frequency distributions of predicted reach-level TN and TP background conditions for the full stream/river network (*20*) in each region. The number of reaches (model prediction points) per region ranges from 25 to 13 603 (average is 4302) (*20*). Within-region variations in yields and concentrations, which extend over an order of magnitude in many regions, reflect local (i.e., reach-level) variations in runoff, deposition, channel size, and basin size. Note that, although basin size is a small positive term in the TP yield model for headwater streams (eq 1), the major effect of increasing basin size on predicted background TP (and its only effect on TN) in larger streams and rivers is negative and is exerted through its relationship to water travel time in the SPARROW model. Travel time influences the cumulative amount of nutrient loss that occurs in stream channels during downstream transport.

Substantial inter-regional variation in predicted background conditions also are evident in Figures 3 and 4. Inter-regional variation in yields and concentrations are the result of the same factors influencing the intra-regional distributions (i.e., runoff, deposition, water travel time, and stream flow) plus the effects of the region indicator variables. The latter are included in the yield models to account for the potential effects of unspecified (i.e., unmeasured) regional characteristics such as soil and vegetation type on nutrient yields in headwater streams. Their lower significance levels in Table 1, however, is evidence that runoff is of paramount importance in explaining regional differences in nutrient yields and concentrations.

The major role of runoff in determining the distributions of TN and TP yield in most regions can be seen by comparing

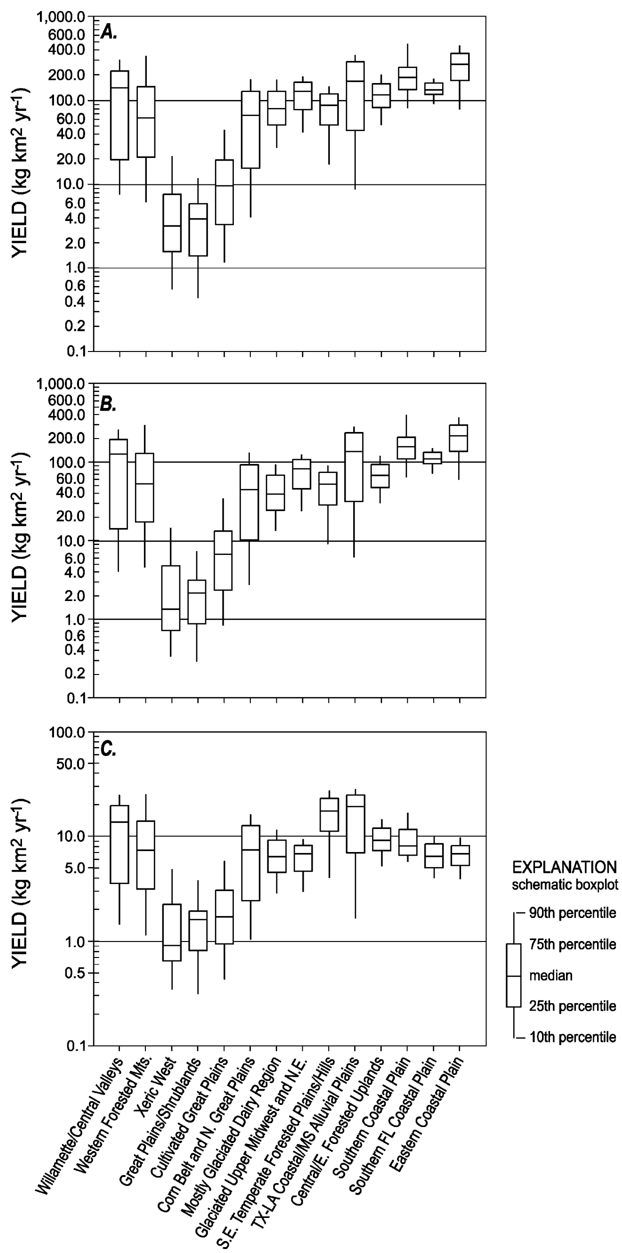

FIGURE 3. Frequency distribution of predicted background nutrient yields by nutrient ecoregion: (A) total nitrogen uncorrected for deposition; (B) total nitrogen corrected for deposition; (C) total phosphorus. Average number of stream reaches (prediction points) per region is 4302.

Figure 3 with the regional distributions of runoff that are presented in box plots in Figure 5. The same regional pattern of low values in the Arid West and Great Plains surrounded by high values in the Far West, Midwest, and East is evident in both figures. Also, in most regions, the width of the distribution of runoff values is reflected in the spread of nutrient yield values in the region. However, the Great Plains Grass and Shrublands (region 4) and TX−LA Coastal and MS Alluvial Plains (region 10), where runoff rates are limited to a narrow range, are clear exceptions. In these regions, the relatively wide variation in both TN and TP yields is due to the presence of large river basins (Missouri and Mississippi, respectively) containing a wide range of river sizes and in-stream travel times. Variation in the amount of in-stream loss (a function of travel time) in these basins results in a broad distribution of predicted yield values.

Another important effect of the geographic pattern in runoff rates is that, contrary to yields, predicted background

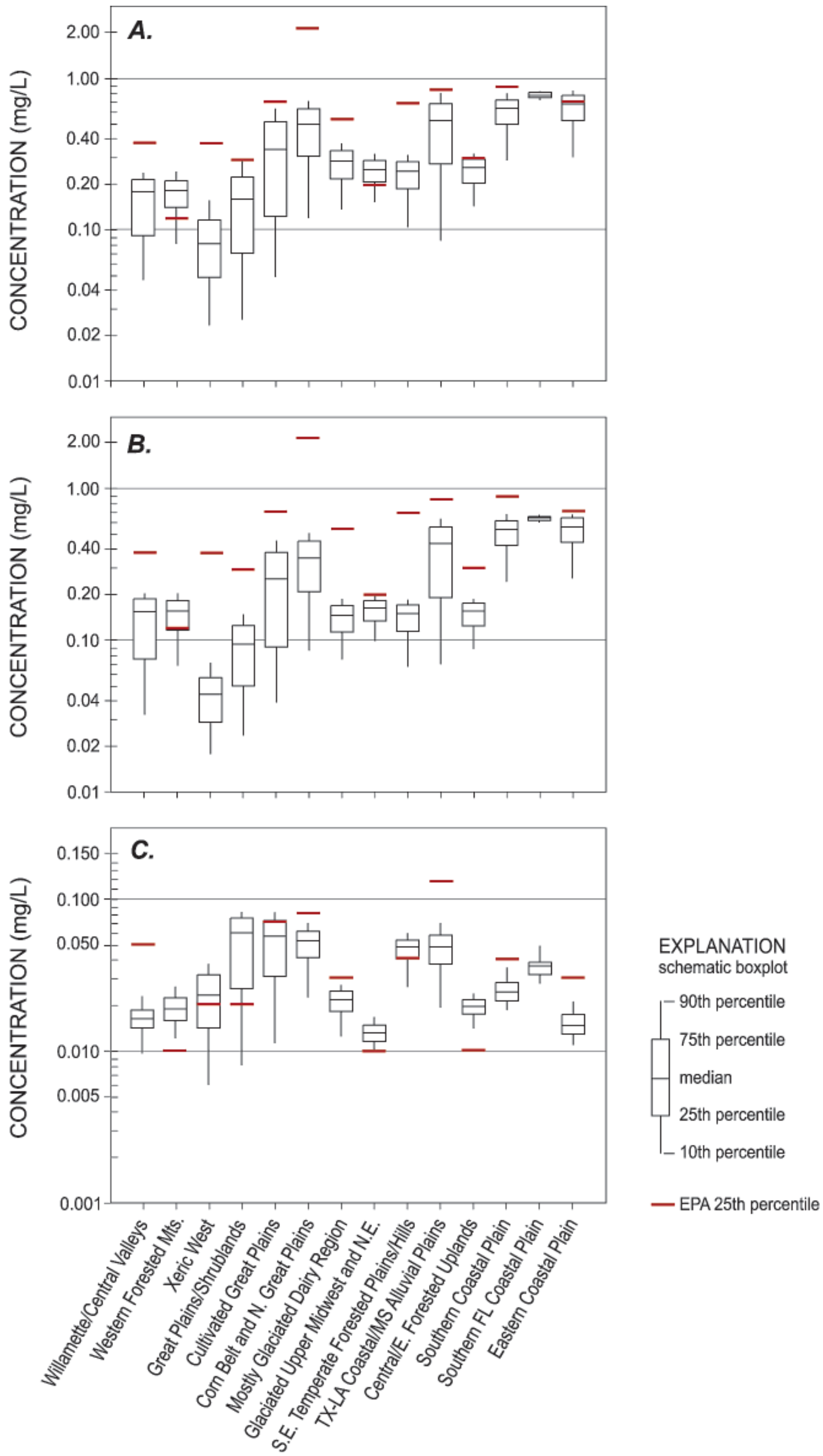

FIGURE 4. Frequency distribution of predicted background nutrient concentrations by nutrient ecoregion: (A) total nitrogen uncorrected for deposition; (B) total nitrogen corrected for deposition; (C) total phosphorus. Average errors (% standard deviation) of regional upper quartile estimates: (A) = 35; (B) = 57; (C) = 34. Red lines show EPA lower-quartile estimates of available monitoring data from developed and undeveloped basins.

TN concentrations in the arid regions (regions 3−5) are only moderately lower than the concentrations seen elsewhere, and background TP concentrations are predicted to be highest in the Great Plains (compare Figures 3 and 4). This is a result of the concentrating effect of lower stream flow on predicted nutrient concentration (as opposed to yield) in the arid regions.

The estimated effects of atmospheric deposition on TN yields and concentrations are evident in comparisons of Figure 3, panel A with panel B, and Figure 4, panel A with panel B. The regional distributions that include N deposition (Figures 3A and 4A) are from 15 to 100% higher than those with deposition removed. The reach-level distribution of percent contribution of atmospheric deposition to TN yield and concentration in each region is given in Figure 6. Although deposition rates are generally higher in the eastern regions, lower runoff (thus lower natural nitrogen inputs) results in a higher percentage contribution of deposition in

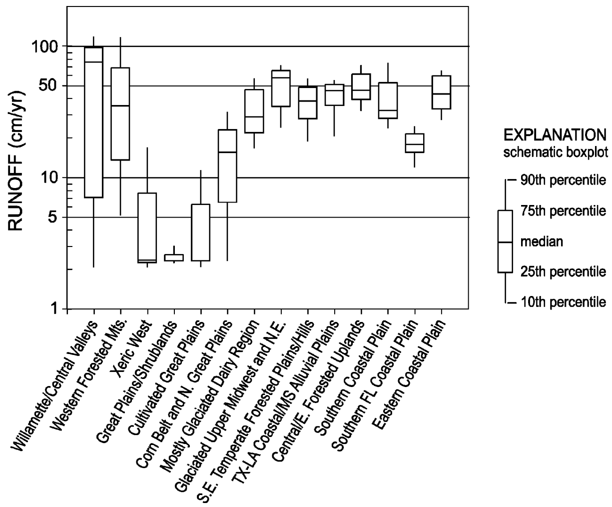

FIGURE 5. Frequency distribution of reach-level mean runoff by nutrient ecoregion (data from ref *25*).

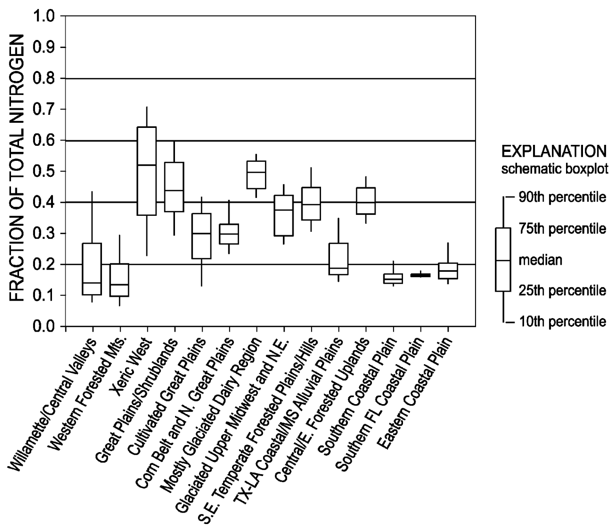

FIGURE 6. Frequency distribution of predicted contribution of atmospheric deposition to background total nitrogen yield and concentration by nutrient ecoregion.

the Arid West. An alternative approach to estimating the contribution of atmospheric deposition to yield is through SPARROW (*23*) regressions of TN yields from developed basins on measures of both natural and cultural nitrogen sources including deposition. Results of this approach for 414 U.S. river basins were summarized by Smith and Alexander (*29*) and show a range in median in-stream atmospheric TN yields from 6 kg km^{-2} yr^{-1} in the Arid West to 124 kg km^{-2} yr^{-1} in the Southeast Coastal Plain drainage. The corresponding range of values for the present study is similar: 1.6 kg km^{-2} yr^{-1} in the Arid West to 99 kg km^{-2} yr^{-1} in the Southeast Coastal Plain.

An overview of predicted background TN and TP concentrations for streams and rivers of the conterminous United States is presented in Figure 7. The maps show reach-level estimated concentration for rivers (eq 3) together with estimated headwater stream concentrations based on yield estimates from eq 1 divided by runoff. River reaches with drainage less than 500 km^2 are omitted from the figures for visual clarity. Concentrations in the omitted reaches are similar to those in the adjacent headwater streams (shaded areas) because in-stream losses during the brief water residence time in these streams is small. Two important features of the maps are worth noting: (i) the local variability in concentration that occurs in regions with moderate to high relief due to local variations in runoff and (ii) the gradual decline in predicted concentration that occurs in most large rivers over long distances. Exceptions occur when nutrient inputs from high-yield tributaries overcome loss processes in the main channel.

Background Concentration Estimates and Nutrient Criteria. A potential application of the results of this study is to provide estimates of background TN and TP concentrations for use in developing regional water quality criteria for nutrients. In recently developed guidance materials (*5*), the U.S. EPA suggests that, for each nutrient region, preliminary criteria for TN and TP concentrations (and other eutrophication related measures) should be set in the range between the upper quartile of reference site data and the lower quartile of all monitoring data. Because of the scarcity of reference site data for several of the regions, however, the EPA has not provided distributions of reference conditions for the nutrient regions. On the basis of analysis of a large combined database of reference site and general monitoring data, the EPA has provided distributions of recent TN and TP concentrations for 13 of the 14 nutrient regions for 1991−1995. Figure 4 compares the lower quartile of EPA-estimated concentrations (shown as red lines) with the upper quartile values from the background TN and TP concentration distributions developed in this study (upper edge of boxes; see also Table S3 in the Supporting Information). The regional background estimates correlate roughly with the EPA estimates for both TN and TP with high concentrations in the Corn Belt and Northern Great Plains and low concentrations in the Western Mountains ($r = 0.63$ and 0.60, respectively). Across all regions, the average upper-quartile value for deposition-corrected background TN is less than half the lower-quartile EPA value (0.29 vs 0.63 mg/L), while the average upper-quartile background TP estimate is almost identical to the average lower-quartile EPA estimate (0.039 vs 0.041 mg/L). Similar distributions of actual stream nutrient conditions to those developed by the EPA were obtained by Dodds et al. (*30*) based on TN and TP records for more than 1000 sites in temperate watersheds of widely varying size and land use in the United States, Europe, and New Zealand. Lower-quartile values for these database were 0.56 mg/L for TN and 0.02 mg/L for TP.

The results in Figure 4 together with those reported by Dodds et al. (*30*) suggest that actual TN concentrations in the nation's streams and rivers exceed natural background levels by a much larger factor than do TP concentrations. On the basis of the distributions developed by Dodds et al. (*30*), the median actual TN concentration (0.89 mg L^{-1}) exceeds the median background (deposition-corrected) TN concentration (0.14 mg L^{-1}) by a factor of 6.4, whereas the median actual TP concentration (0.045 mg L^{-1}) exceeds the median background TP concentration (0.023 mg L^{-1}) by a factor of less than 2.0. This difference is consistent with the fact that estimated cultural loading (terrestrial and atmospheric) of nitrogen to U.S. watersheds exceeds the cultural phosphorus loading by a factor of about 13 by weight (*31*), as compared to the median background TN/TP ratio of 6.1 estimated here. A likely explanation for the relatively smaller elevation of actual TP concentrations over background levels is the fact that pollution controls have resulted in a significant reduction in TP concentrations in streams nationwide over the past 2−3 decades, while TN concentrations have generally increased or remained stable (*31, 32*). Also, the retention of phosphorus in large reservoirs is omitted from the TP transport model applied here in order to represent predevelopment conditions (see Methods). As a result, estimated background TP yields and concentrations in some streams and rivers are higher than they would be in the presence of

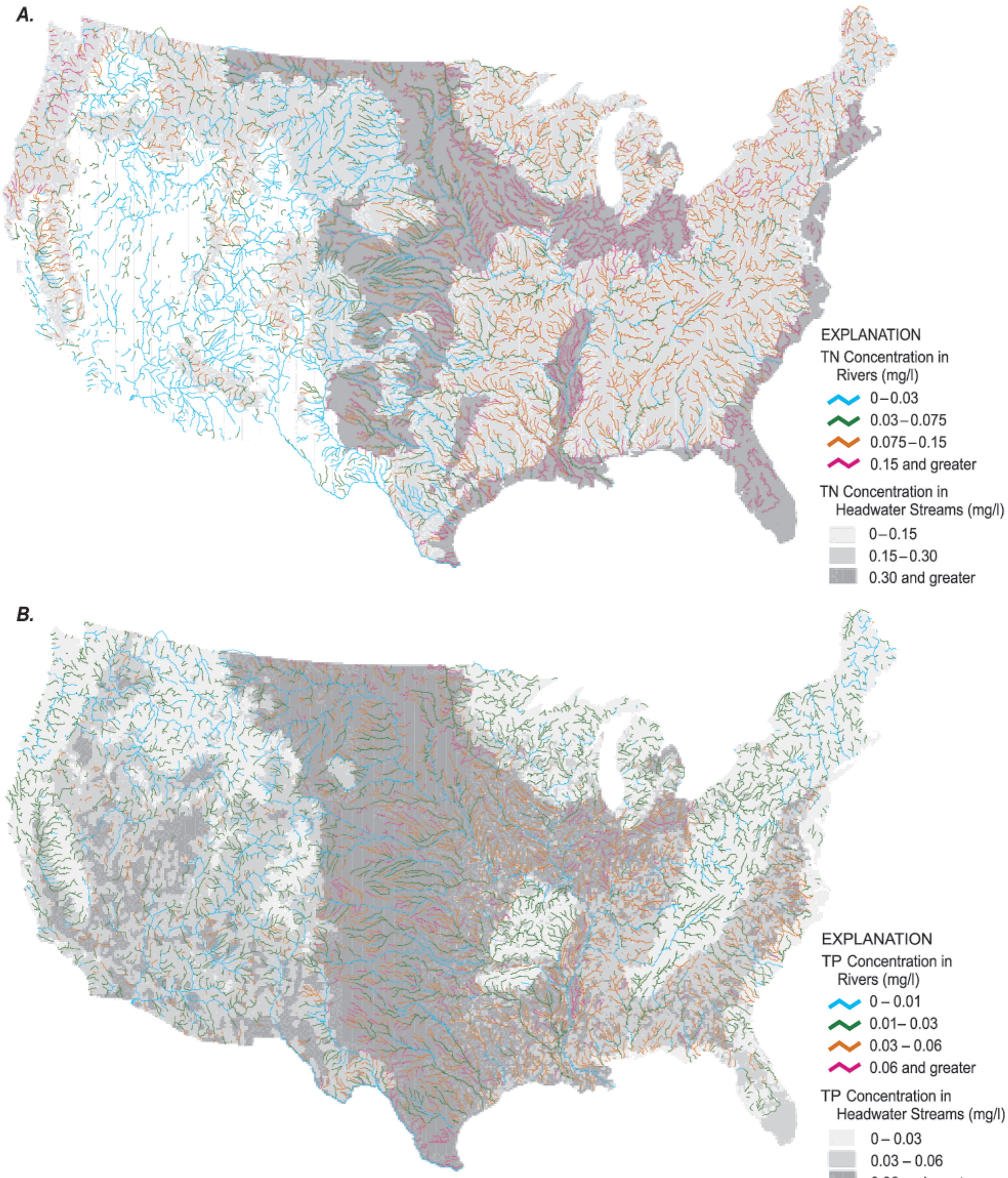

FIGURE 7. Model predictions of background concentrations of nutrients in headwater streams (shaded areas) and streams and rivers with drainage area greater than 500 km^2: (A) total nitrogen corrected for atmospheric deposition; (B) total phosphorus.

existing large reservoirs (see Table S6 in the Supporting Information).

It is desirable that natural background conditions be considered in setting nutrient criteria given that natural factors affect the potential for achieving water quality goals for nutrients. Regionalizing the criteria development process provides one means for accounting for some of the nationwide variation in background conditions (*6*). The results of this study, however, indicate that as much as an order of magnitude of variation in the natural background concentration of TN and TP exists within the boundaries of many of the EPA nutrient ecoregions. Indeed, large variation in background levels appears to occur over short distances in many regions due to elevation-related variation in runoff and differences in cumulative in-stream nutrient loss at the junctions of small tributaries and large rivers. As a result, predicted background TP concentrations in many stream and river segments exceed the EPA-proposed criteria for their region based on lower-quartile values (an estimated 52% of reaches nationwide; see Table S5 in the Supporting Information). Such localized variation in background concentrations argues against the use of arbitrary quantiles (e.g., lower quartiles) of concentration distributions for large regions as a basis for setting water quality criteria. Subdivision of the nutrient ecoregions may permit development of more locally valid criteria where there are adequate monitoring stations and data. Models of background nutrient concentration, such as those developed here, can assist the criteria development process where monitoring data are sparse. However, the prediction error of the models increases, in general, as the region in question (i.e., number of prediction points) gets smaller. The mean error (percent standard deviation) for individual reach-level predictions in this study is 53% for TN and 51% for TP; the corresponding mean error values for the current regional quartile estimates are 35% and 34% (see Figure 4 and Tables S3 and S4 in the Supporting Information). The biggest improvements in model performance will likely come from (i) elucidation and incorporation in the models of the individual environmental factors represented by the "region-specific factors" and (ii) development of region-specific models based on data from additional reference sites.

Acknowledgments

We greatly appreciate reviews of this paper by our colleagues Jeffrey Stoner, Gregory Clark, David Mueller, and Robert Hirsch.

Supporting Information Available

Information on water quality reference sites, statistical methods, and model accuracy, and a more detailed presentation of results of the study. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Leopold, L. B. *Geol. Surv. Circ.* (*U.S.*) **1962**, *No. 460-A*.
(2) Meybeck M. *Am. J. Sci.* **1982**, *282*, 401–450.
(3) Vitousek, P. M.; Aber, J. D.; Howarth, R. W.; Likens, G. E.; Matson, P. A.; Schindler, D. W.; Schlesinger, W. H.; Tilman, D. G. *Ecol. Appl.* **1997**, *7*, 737–750.
(4) Dole, R. B. *U.S. Geol. Surv. Water-Supply Pap.* **1909**, *No. 236*.
(5) U.S. Environmental Protection Agency. *Nutrient Criteria: Technical Guidance Manual*; *Rivers and Streams*; EPA 822B-00-002; U.S. Environmental Protection Agency: Washington, DC, 2000.
(6) Dodds, W. K.; Welch, E. B. *J. North Am. Benthol. Soc.* **2000**, *19*, 186–196.
(7) Dodds, W. K.; Smith, V. H.; Lohman, K. *Can. J. Fish. Aquat. Sci.* **2002**, *59*, 65–74.
(8) Lewis, W. M., Jr.; Melack, J. M.; McDowell, W. H.; McClain, M.; Richey, J. E. *Biogeochemistry* **1999**, *46*, 149–162.
(9) Yoder, C. O.; Rankin, E. T. *Environ. Monit. Assess.* **1998**, *51*, 61.
(10) Clark, G. M.; Mueller, D. K.; Mast, M. A. *J. Am. Water Res. Assoc.* **2000**, *36*, 849–860.
(11) Dodds, W. K.; Blair, J. M.; Henebry, G. M.; Koelliker, J. K.; Ramundo, R.; Tate, C. M. *J. Environ. Qual.* **1996**, *25*, 973–981.
(12) Holloway, J. M.; Dahlgren, R. A.; Hansen, B.; Casey, W. H. *Nature* **1998**, *395*, 785–788.
(13) Howarth, R. W.; Billen, G.; Swaney, D.; Townsend, A.; Jaworski, N.; Lajtha, K.; Downing, J. A.; Elmgren, R.; Caraco, N.; Jordan, T.; Berendse, F.; Freney, J.; Kudeyarov, V.; Murdoch, P.; Zhao-liang, Z. *Biogeochemistry* **1996**, *35*, 75–139.
(14) Sauer, T. J.; Alexander, R. B.; Brahana, J. V.; Smith, R. A. The importance and role of watersheds. In *Nitrogen in the Environment: Sources, Problems, and Management*; Follett, R. F., Hatfield, J. L., Eds.; Elsevier Science Publishers: Dordrecht, The Netherlands, 2001.
(15) Peterson, B. J.; Wollheim, W. M.; Mulholland, P. J.; Webster, J. R.; Meyer, J. L.; Tank, J. L.; Marti, E.; Bowden, W. B.; Valett, H. M.; Hershey, A. E.; McDowell, W. H.; Dodds, W. K.; Hamilton, S. K.; Gregory, S.; Morrall, D. D. *Science* **2001**, *292*, 86.
(16) Alexander, R. B.; Smith, R. A.; Schwarz, G. E. *Nature* **2000**, *403*, 758–761.
(17) Perakis, S. S.; Hedin, L. O. *Nature* **2002**, *415*, 416–419.
(18) Lewis, W. M., Jr. *Biogeochemistry* **2002**, *57/58*, 375–385.
(19) Gilliom, R. J. *Water Resour. Res.* **1981**, *17*, 410.
(20) Alexander, R. B.; Brakebill, J. W.; Brew, R. E.; Smith, R. A. *ERF1—Enhanced River Reach File 1.2*; Open-File Report 99-457; U.S. Geological Survey: Reston, VA, 1999.
(21) Omernik, J. A. Draft Aggregations of Level III Ecoregions for the National Nutrient Strategy. 2000, http://www.epa.gov/ost/standards/ecomap.html.
(22) Prairie, Y. T.; Kalff, J. *Water Resour. Bull.* **1986**, *22*, 465–470.
(23) Smith, R. A.; Schwarz, G. E.; Alexander, R. B. *Water Resour. Res.* **1997**, *33*, 2781–2798.
(24) Cohn, T. A.; Delong, L. L.; Gilroy, E. J.; Hirsch, R. M.; Wells, D. K. *Water Resour. Res.* **1989**, *25*, 937–942.
(25) Gebert, W. A.; Graczyk, D. J.; Krug, W. R. *Average annual runoff in the United States, 1951–80*, Hydrologic Investigations Atlas HA-710, scale 1:7,500,000; U.S. Geological Survey: Reston, VA, 1987.
(26) Cobb, E. D.; Biesecker, J. E. *Geol. Surv. Circ.* (*U.S.*) **1971**, *No. 460-D*.
(27) Nolan, J. V.; Brakebill, J. W.; Alexander, R. B.; Schwarz, G. E. *ERF1–2—Enhanced River Reach File Version 2.0*; Open-File Report 02-40; U.S. Geological Survey: Reston, VA, 2002.
(28) Downing, J. A.; McClain, M.; Twilley, R.; Melack, J. M.; Elser, J.; Rabalais, N. N.; Lewis, W. M., Jr.; Turner, R. E.; Corredor, J.; Sota, D.; Yanez-Arancibia, A.; Kopaska, J. A.; Howarth, R. W. *Biogeochemistry* **1999**, *46*, 109–148.
(29) Smith, R. A.; Alexander, R. B. Sources of Nutrients in the Nation's Watersheds. In *Managing Nutrients and Pathogens from Animal Agriculture*, Proceedings from the Natural Resource, Agriculture, and Engineering Service Conference for Nutrient Management Consultants, Extension Educators, and Producer Advisors, March 28–30, 2000, Camp Hill, PA.
(30) Dodds, W. K.; Jones, J. R.; Welch, E. B. *Water Res.* **1998**, *32*, 1455–1462.
(31) Smith, R. A.; Alexander, R. B.; Wolman, M. G. *Science* **1987**, *235*, 1607–1615.
(32) Smith, R. A.; Alexander, R. B.; Lanfear, K. J. In *National Water Summary 1990–91*; Paulson, R. W., et al., Eds.; U.S. Geological Survey Water Supply Paper 2400; U.S. Geological Survey: Reston, VA, 1993; pp 111–140.

Received for review March 27, 2002. Revised manuscript received March 14, 2003. Accepted March 24, 2003.

ES020663B