

Streamflow-induced variations in nitrate flux in tributaries to the Atlantic Coastal Zone

RICHARD B. ALEXANDER¹, PETER S. MURDOCH² &
RICHARD A. SMITH¹

¹*U.S. Geological Survey, 12201 Sunrise Valley Drive, 410 National Center, Reston, Virginia 22092;* ²*U.S. Geological Survey, 425 Jordan Road, Troy, New York 12180*

Received 6 March 1995; accepted 30 October 1995

Key words: Atlantic estuaries, climate change, climatic variability, coastal management, nitrate flux, seasonal variability

Abstract. Streamflow-related variability in nutrient flux represents an important source of uncertainty in managing nutrient inputs to coastal ecosystems. Quantification of flux variability is of particular interest to coastal resource managers in adopting effective nutrient-reduction goals and monitoring progress towards these goals. We used historical records of streamflow and water-quality measurements for 104 river monitoring stations in an analysis of variability in annual and seasonal flux of nitrate to the Atlantic coastal zone. We present two measures of temporal flux variability: the coefficient of variation (CV) and the exceedence probability (EP) of 1.5 times the median flux. The magnitude of flux variations spans a very wide range and depends importantly upon the season of year and the climatic and land-use characteristics of the tributary watersheds. Year-to-year variations (CV) in annual mean flux range over two orders of magnitude, from 3–200% of the long-term mean flux, although variations more typically range from 20–40% of the long-term mean. The annual probability of exceeding the long-term median flux by more than 50% (EP) is less than 0.10 in most rivers, but is between 0.10 and 0.35 in 40% of the rivers. Year-to-year variability in seasonal mean flux commonly exceeds that in annual flux by a factor of 1.5 to 4. In western Gulf of Mexico coastal rivers, the year-to-year variability in the seasonal mean flux is larger than in other regions, and is of a similar magnitude in all seasons. By contrast, in Atlantic coastal rivers, the winter and spring seasons, which account for about 70% of the annual flux, display the smallest relative variability in seasonal mean flux. We quantify the elasticity of nutrient flux to hypothetical changes in streamflow (i.e., the percent increase in flux per percentage increase in mean discharge) to allow the approximation of flux variability from streamflow records and the estimation of the effects of future climatically-induced changes in streamflow on nutrient flux. Flux elasticities are less than unity (median = 0.93%) at most stations, but vary widely from 0.05% to 1.59%. Elasticities above unity occur most frequently in the largest rivers and in rivers draining the arid portions of the western Gulf of Mexico Basin. Historical flux variability and elasticity generally increase with the extent of arid conditions and the quantity of nonurban land use in the watershed. We extend the analysis of flux variability to examine several case studies of highly unusual meteorological events capable of significantly elevating nitrate flux and degrading estuarine ecology.

Introduction

Coastal resource managers have a need to define the capacity of coastal ecosystems to receive nitrogen inputs without degradation. In simplest terms,

management goals might be stated as the acceptable mean flux of nitrogen and other nutrients to coastal waters. However, nutrient flux in fluvial systems can vary widely at both short and long time scales, with much of the variation intrinsically linked to temporal fluctuations in streamflow and climate. Moreover, there is ample evidence that temporal variations in nutrient flux have significant biological effects (Queguiner & Treguer 1986; Rosenberg et al. 1988; Brockmann & Eberlein 1986; Franz 1986; Zubkoff & Warinner 1977). Although estimates of mean flux to the North Atlantic (see, for example, Howarth and others, in press) provide baseline information for developing management goals, resource managers also need quantification of the temporal variability in nutrients to establish effective nutrient-reduction goals.

Temporal variability in nutrient flux to the coastal zone presents dual problems for managers. First, it increases the difficulty of monitoring nutrient flux to confirm the effects of management actions. In rivers with large natural flux variations, management plans need to provide adequate monitoring to determine if management goals are being met. Second, the biological significance of flux variability implies that management goals may need to explicitly account for that variability. This may include the use of more stringent controls in estuarine tributaries with large natural flux variations to ensure that biologically-relevant nutrient reductions can be achieved. A logical starting point for dealing with both problems is to develop as thorough a characterization of flux variability as is possible with available records.

This paper quantifies streamflow-induced seasonal and annual variability in nitrate flux based on data from 104 Atlantic coastal rivers and several case studies of large, infrequent meteorological events in Atlantic estuaries. Following a description of methods, we discuss four aspects of flux variability. We first present long-term annual estimates of nitrate flux, and quantify the seasonal distribution of the annual flux. Secondly, we quantify streamflow-induced variations in annual and seasonal flux over the last two decades using two measures of variability: the coefficient of variation (CV) and the exceedence probability (EP) of 1.5 times the median flux. These measures quantify natural variations in flux that could potentially undermine the effects of nutrient controls on estuarine health and complicate the measurement of progress in pollution control. Thirdly, we quantify the sensitivity of nutrient flux to hypothetical changes in streamflow. Estimates of the sensitivity, or "elasticity," of flux provide an efficient method for estimating the water-quality effects of future streamflow changes. Finally, we extend the analysis of flux variability to quantify the magnitude of increases in nitrate flux associated with large, highly unusual meteorological events. Three case studies illustrate

the effects of these infrequent, extreme events on nitrate flux and estuarine ecology.

Methods: estimates of annual and seasonal flux

Coastal rivers and regions

We selected 104 river locations (Figure 1), monitored as part of the U.S. Geological Survey's (USGS) National Stream Quality Accounting Network [NASQAN; see Langford & Kapinos (1979) for a description of the network], to characterize the nitrate flux from eight major regional drainage areas in the Atlantic coastal zone over the period of the 1970's and 1980's. These stations are located on the "fall line" of rivers of the eastern and Gulf of Mexico states of the United States. In one case where a fall-line station lacked sufficient data (the Atchafalaya River), a station on an upstream tributary (the Red River) was selected as an alternative. The variability and magnitude of flux in the Atchafalaya River could be expected to differ from that in the Red River because approximately one third of the Mississippi River's flow is diverted annually into the Atchafalaya Basin. We present separate analyses of flux for three of the 104 rivers (the St. Lawrence, Mississippi, and Red rivers) because of their comparatively large drainage areas. Collectively, the rivers used in this analysis drain more than 95% of the total U.S. continental drainage to the Atlantic and Gulf of Mexico, and include small portions of drainage to the Atlantic from Canada (the St. Lawrence River) and Mexico (the Rio Grande River). Selected physical and cultural characteristics, including drainage area, mean runoff, and population density are presented in Table 1 for the eight regional drainage areas of the Atlantic coastal zone.

Chemical data

Samples were collected according to NASQAN protocols and analyzed for nutrients from the mid 1970s to 1989 [see Langford & Kapinos (1979) for a summary of the network protocols]. Depth- and width-integrated samples provide a representative sample of water in the cross-sections of the monitored rivers. Samples were chilled to approximately 4 °C and promptly analyzed in one of two centralized laboratories operated by the USGS. From October, 1980 to 1989, nutrient samples were stored in amber bottles and treated with the biocide preservative mercuric chloride.

Samples were analyzed for dissolved nitrate-nitrite (using 0.45 micron filtration) from 1979 to 1989 and for total nitrate-nitrite from the mid 1970s to 1981 at most stations. For purposes of flux estimation, a complete record of

Table 1. Selected physical and cultural characteristics of the monitored drainage areas of five coastal regions and three rivers of the Atlantic coastal zone. Regional quartiles of the distribution of monitoring stations estimates are reported.

Region/river	Number stations*	Drainage Area (km ²)			Runoff (m ³ /day/km ²)			Population density (#/km ²)		
		25th	50th	75th	25th	50th	75th	25th	50th	75th
St. Lawrence R.	1	-	784,171	-	-	880	-	-	27	-
North Atlantic	20	640	2,753	13,193	1,520	1,810	1,960	7	51	227
Mid Atlantic	14	318	3,183	16,765	1,030	1,150	1,490	29	59	377
South Atlantic	19	1,913	8,354	13,791	890	1,000	1,080	15	34	57
Eastern Gulf of Mexico	29	976	2,113	10,763	870	1,690	1,910	14	24	33
Mississippi R.	1	-	2,965,388	-	-	440	-	-	23	-
Red R.	1	-	126,050	-	-	270	-	-	9	-
Western Gulf of Mexico	15	1,908	13,642	45,103	160	410	740	7	19	71

* Basin characteristics data are not reported for four basins with indeterminate drainage.

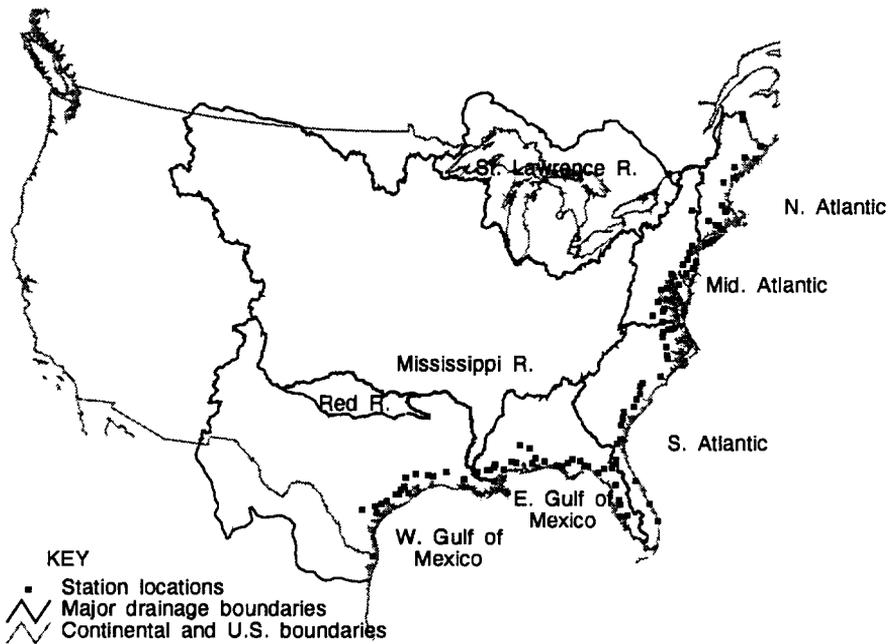


Figure 1. Locations of 104 coastal NASQAN monitoring stations and eight regional drainage divisions of the Atlantic coastal zone. The highlighted boundaries show the approximate extent of the total monitored drainage in the United States, Canada, and Mexico.

dissolved nitrate-nitrite was assembled, spanning the period of the mid-1970s to 1989. Record extension methods (Hirsch 1982), that maintain the variance of the original records, were employed to estimate dissolved nitrate-nitrite for the pre-1979 period. Pairs of total and dissolved nitrate-nitrite from the 1979–81 period were used to estimate the correlation of the data. Measurements of dissolved and total nitrate-nitrite typically displayed a high degree of correlation (Pearson $r > 0.90$ at most stations). Nondetected values, which typically constitute less than about 10% of the observations, were assigned one half of the reporting limit for purposes of flux estimation.

The NASQAN sampling frequency was monthly from the mid-1970s to 1981 and bimonthly or quarterly at most sites from 1982 to 1989. More frequently collected data exist for a small number of stations; however, no more than four samples per month were used in this analysis. In cases of more frequent data, the month is divided into four equal time periods, and the value closest to the middle of each period (and paired with discharge) was selected for use.

Annual and seasonal flux estimation methods

We used log-linear regression-based flux models, or “rating-curve” techniques, to estimate mean annual and seasonal flux at each station. By relating the periodically-collected instantaneous nitrate-nitrite flux (computed as the product of concentration and discharge) to discharge, season, and time, these models provide an efficient technique for using more complete daily flow records to predict daily values of flux. Log-linear models of this type have been found to provide satisfactory fit to many water-quality variables (Cohn et al. 1992). Moreover, the statistical properties of the estimates are well understood due to considerable theoretical development and evaluation (Bradu & Mundlak 1970; Ferguson 1986; Koch & Smillie 1986; Cohn et al. 1989; Gilroy et al. 1990).

Periodic measurements of flux are related to a possible set of five explanatory variables. The full model is of the form

$$\ln(l) = \beta_0 + \beta_1 t + \beta_2 \sin(2\pi t) + \beta_3 \cos(2\pi t) + \beta_4 \ln(q) + \beta_5 (\ln(q))^2 + \varepsilon \quad (1)$$

where l is the instantaneous flux of nitrate-nitrite, t is decimal time, q is instantaneous discharge, ε is the sampling and model error assumed to be independent and identically distributed, \ln is the natural logarithm function used to improve the linearity of the relation, and \sin and \cos are trigonometric functions that jointly approximate seasonal (cyclical) variations in flux. For a single nitrate-nitrite record at a station, fifteen possible models (seasonal terms enter and exit as a pair) can be fit to the observed data. Of these models, the one with the minimum value of prediction error sum of squares (PRESS) is considered to provide the “best” fit (Montgomery & Peck 1982). Samples sizes commonly range from 62 to 117 observations (median = 83).

We estimated daily flux from 1970 to 1988 at each station by substituting daily mean values of discharge into the selected model. For the full regression model, the predicted daily flux (L) for the i th day of the j th season and k th year expressed in original units is written as

$$L_{ijk} = \exp[b_0 + b_1 T' + b_2 \sin(2\pi T_{ijk}) + b_3 \cos(2\pi T_{ijk}) + b_4 \ln Q_{ijk} + b_5 (\ln Q_{ijk})^2] \cdot \exp[g_{ijk}^m] \quad (2)$$

where Q is the daily mean discharge, T' is decimal time fixed to mid 1988, T is decimal time associated with daily mean discharge, and g^m is the transformation bias-correction factor associated with the minimum variance unbiased estimator (MVUE) of Bradu & Mundlak (1970) as described in Cohn et al. (1989) and Gilroy et al. (1990). Setting T' to 1988 eliminates the influence of year-to-year variability in nutrient sources on estimates of flux variability.

Thus at a given station, variability in flux for purposes of this analysis is solely a function of seasonal variations in nutrient sources and annual and seasonal variations in discharge over the 19-year period. Differences in flux between stations reflect the effects of anthropogenic and natural sources of nutrients based on 1988 conditions.

We used values of daily flux to obtain estimates of annual and seasonal mean flux for both the full time period and each year. We computed a “long-term” mean flux, based on the full time period, and its seasonal components to describe geographic and seasonal differences in flux among the various coastal regions and rivers. The long-term mean standardizes station flux and streamflow conditions to the 1970–88 period, thereby avoiding temporal differences arising from the varying lengths of the station chemical records. This standardization also fixes nutrient sources to 1988 levels. We used separate yearly estimates of the annual and seasonal mean flux to describe variability caused by year-to-year variations in annual and seasonal discharge.

Estimates of the long-term mean annual flux (L^A) were computed for each station as

$$L^A = \frac{\sum_{k=1}^{19} \sum_{j=1}^4 \sum_{i=1}^{N_{jk}} L_{ijk}}{N} \quad (3)$$

where N is the total number of daily flux estimates over the 19 year period, and N_{jk} is the number of daily flux values in the j th season and k th year. Four seasons are defined as follows: winter (December through February), spring (March through May), summer (June through August), and fall (September through November).

Long-term estimates of the seasonal contribution to the total flux for each season and station expressed as percent (S_j) were computed as

$$S_j = \frac{\sum_{k=1}^{19} \sum_{i=1}^{N_{jk}} L_{ijk}}{\sum_{j=1}^4 \sum_{k=1}^{19} \sum_{i=1}^{N_{jk}} L_{ijk}} \times 100 \quad (4)$$

For analyzing temporal variations in flux, seasonal and annual time series of 19 years length were generated. The annual mean flux for the k th year for each station (L_k^A) was computed as

$$L_k^A = \frac{\sum_{j=1}^4 \sum_{i=1}^{N_{jk}} L_{ijk}}{N_k} \quad (5)$$

where N_k is the number of observations in the k th year. The seasonal mean flux for the j th season and k th year for each station (L_{jk}^S) was computed as

$$L_{jk}^S = \frac{\sum_{i=1}^{N_{jk}} L_{ijk}}{N_{jk}} \quad (6)$$

Historical variability in annual and seasonal flux

We used two measures to quantify year-to-year variations in annual and seasonal flux at each station resulting from observed fluctuations in discharge during the 19-year period, 1970–88. We first used the coefficient of variation or CV (the quotient of the standard deviation and mean) of the time series L_k^A and L_{jk}^S as a standardized measure of the relative magnitude of discharge-related variations in flux. Secondly, we separately estimated the annual and seasonal exceedence probability (EP), the probability that the annual and seasonal mean flux exceeds the long-term median annual and seasonal flux by a factor of 1.5, respectively. Using cumulative empirical distribution functions of annual (L_k^A) and seasonal (L_{jk}^S) mean flux, the EP was estimated as the linearly-interpolated Cunnane (1978) plotting position frequency corresponding to 1.5 times the long-term median annual and seasonal flux.

In estimating values of CV and EP, we used Monte Carlo methods to simulate variations in annual and seasonal flux related to uncertainty in the estimated model parameters. For each station, we generated 1000 time series of annual and seasonal flux from which the mean CV and EP were computed. Each year's annual and seasonal flux is lognormally distributed with mean L_k^A and L_{jk}^S and standard deviation σ_k^A and σ_{jk}^S , respectively. The standard deviation of annual and seasonal flux is determined from MVUE estimates of the mean square error of sums of daily flux (Gilroy et al. 1990). Log-transformed estimates of the moments were obtained from Loucks et al. (1981). Note that the estimates of the mean square errors in annual and seasonal flux do not account for errors related to mis-specification of the flux model.

Elasticity of annual and seasonal flux

We used the flux regressions in equation 2 to describe the sensitivity of flux to prescribed changes in discharge at each station. We expressed sensitivity in terms of the elasticity of nitrate flux with respect to discharge by computing the percent increase in flux resulting from a 1% increase in mean annual discharge. Elasticity values of one indicate a proportional response of flux to changes in streamflow. Seasonal regression model terms were held constant to mid 1988 in computing these estimates. To assess the consistency of flux elasticity over a range of streamflow conditions, we also computed the flux elasticities associated with a 1% increase in the seasonal mean discharge. Seasonal terms in equation 2 were set to the midpoint of each respective season in making these computations.

Plotting of station statistics

The station flux statistics, including CV, EP, and elasticity, are graphed in box and whisker plots (Tukey 1977) for the five coastal regions and as single points for each of the three large rivers (see example in Figure 2). Each box graphs the station quartiles, with lower and upper edges representing the lower and upper quartiles (25th and 75th percentiles), respectively. The midline of each box plots the median. The upper and lower whiskers are drawn to the station value within ± 1.5 times the interquartile range (IQR), respectively. Station values exceeding 3 times the IQR appear as a “x”.

Long-term mean annual nitrate flux

Mean annual flux

Annual nitrate flux (equation 3) for the five regions and three rivers of the eastern U.S. (Figure 2a) show values ranging over five orders of magnitude (from less than 10 to nearly one million Mg/yr or metric tons/yr). Drainage basin size accounts for a significant portion of the differences in flux among the regions. The Mississippi and St. Lawrence rivers as well as many of the large rivers of the Mid Atlantic region display the largest nitrate flux ranging from about 10,000 to nearly one million Mg/yr.

Errors in the estimates of long-term mean annual flux typically range from 2 to 5 percent with a station median of about 3 percent. These error estimates assume a proper specification of the flux-discharge models.

Mean annual yield

To highlight geographic differences in mean annual flux related to climate and nitrogen sources rather than river size, we adjusted the station flux estimates for drainage basin size by dividing by the basin area to produce estimates of yield expressed as kilograms per square kilometer per year.

Annual nitrate yield for the five regions of the eastern U.S. (Figure 2b) display an approximate order-of-magnitude difference in values among streams in each region. As an exception, the Western Gulf of Mexico displays a two order of magnitude range due to the wide diversity of climatic conditions in this region. Median yields ranged from a high of 355 kg/km²/yr in the Mid Atlantic region to a low of 49 kg/km²/yr in the Western Gulf of Mexico region. In addition to the Western Gulf of Mexico, the North and Mid Atlantic, the most industrialized areas of the eastern seaboard (see Table 1), display the greatest variability in yield among stations. These differences

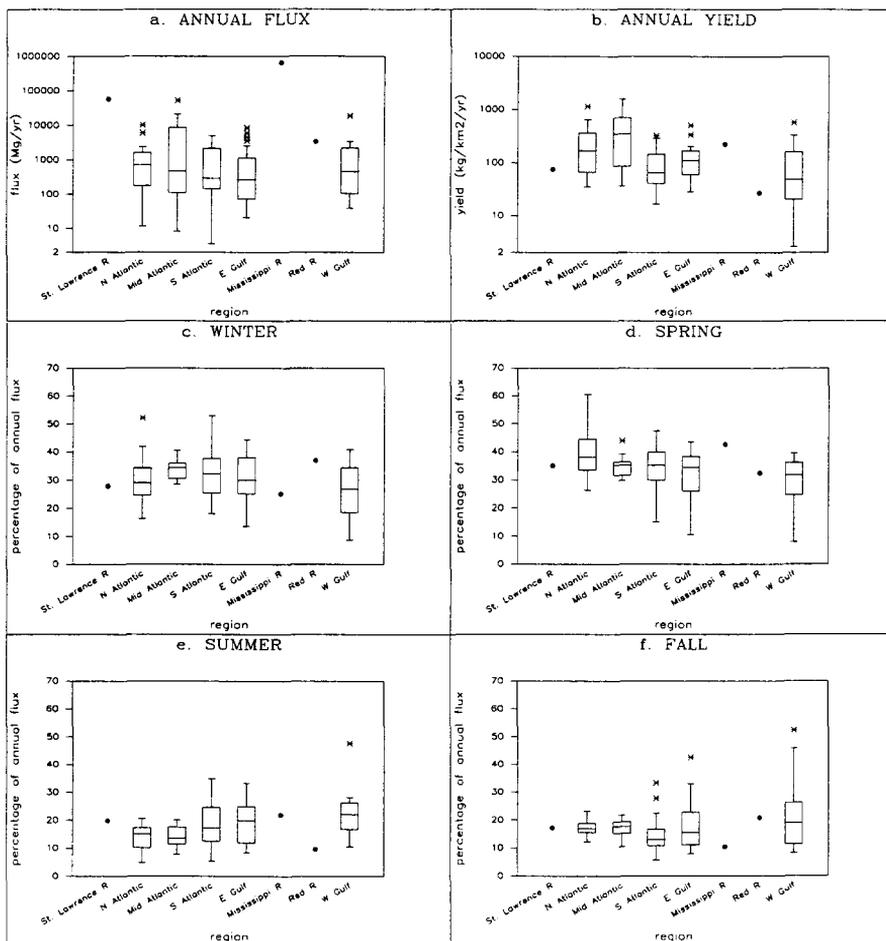


Figure 2. Distribution of (a) long-term mean annual nitrate flux, (b) long-term mean annual nitrate yield, and seasonal contributions to annual flux in percent for (c) winter, (d) spring, (e) summer, and (f) fall by regional drainage divisions of the Atlantic coastal zone. Refer to the methods section for an explanation of the box and whisker plots. The solid points describe the flux statistics for the three largest rivers.

likely reflect differences among stations in the magnitude of agricultural and point sources of nitrogen. The wide diversity among Western Gulf of Mexico stations relates predominantly to large differences in runoff. The smallest differences in yield among stations occur in the South Atlantic and the Eastern Gulf of Mexico regions. The annual yield in the Red River (27 kg/km²/yr) was very similar to the most arid basins of the Western Gulf of Mexico region, whereas the yield for the Mississippi River (224 kg/km²/yr) was similar to

those found in the industrialized eastern seaboard basins. The St. Lawrence yield of $75 \text{ kg/km}^2/\text{yr}$ was in the moderate to low range.

These estimates of yield reveal significant variations in annual nitrate yields between rivers and regions of the eastern United States. Thus, any individual estuary may receive annual loadings that significantly differ from the regional average.

Seasonal distribution of annual flux

Station estimates of the seasonal contributions to annual flux (equation 4) are shown separately by region in Figure 2 (c–f). Relatively few differences exist in the winter percentage of the annual flux among the regions, but other seasons display notable regional differences. With the exception of the Western Gulf of Mexico, the winter and spring seasons collectively account for 63 to 69 percent of the annual flux from most stations in the regions. The North Atlantic and the Mississippi River show the highest winter/spring percentages of any regions, reflecting the cyclical effects of precipitation and snowmelt. By contrast, the Eastern and Western Gulf of Mexico coast basins had more uniform seasonal contributions to annual flux reflecting similarities in seasonal precipitation in the region. The St. Lawrence River has one of the lowest winter/spring percentages most likely due to the dampening of seasonal variability by the Great Lakes. The Mississippi River had, by far, the highest percentage contribution in the spring season (43%) and the lowest winter and fall contributions (25% and 10%, respectively).

These seasonal estimates suggest that nitrate flux varies considerably during the year in some coastal regions. In general, the most pronounced seasonal variations occur in Atlantic coastal rivers where the winter and spring seasons account for about 70% of the annual flux. By contrast, few seasonal differences exist in nitrate yields in the Eastern and Western Gulf of Mexico coastal rivers.

Available data for coastal rivers of other Atlantic regions indicate many similarities with the seasonal distributions of yield for U.S. rivers. Two years of data for major rivers entering the North Sea indicate that the spring season (February to April) accounts for 41% of the annual total nitrogen flux (G. Billen 1994, written comm.). Nitrogen yields from the Vistula and Odra river basins in Poland were the largest during spring snowmelt and fall rains (Taylor 1984), similar to that observed in streams of the northeastern U.S. In contrast, two years of data from the Amazon River at Obidos revealed similar seasonal exports during the winter, spring, and summer, whereas fall exports were approximately one half of those in other seasons (Salatl et al. 1982). These estimates are consistent with a general geographic pattern of

fewer seasonal differences in nitrogen flux and runoff in warmer as compared to colder climates.

Variability in annual and seasonal nitrate flux

Using the three statistics of CV, EP, and flux elasticity, we describe the magnitude of discharge-related variations in seasonal and annual flux for tributaries to the Atlantic coastal zone. We also examine the possible relation of watershed characteristics to observed geographic differences in flux variability.

Historical variability in annual and seasonal flux

We present two measures of historical variability in flux. The CV statistic provides a conventional measure of relative variability, which complements the widely available CV statistics on annual and seasonal streamflow. The EP statistic is designed to more specifically address how the magnitude of discharge-induced variations in flux compares with management goals targeting reductions in annual or seasonal mean nutrient flux. We selected a 50% exceedence threshold to approximately correspond with recent management recommendations for two major northwestern Atlantic estuaries. A recent nutrient management goal adopted for the Chesapeake Bay calls for a 40 percent reduction in mean flux by the year 2000 (Thomann et al. 1994). In addition, management recommendations for the Neuse River estuary, a major tributary to the Pamlico Sound, prescribe nitrogen reductions of 30 to 70 percent (Paerl 1987; H.W. Paerl 1995, written communication). Thus, the EP statistic provides an estimate of how frequently discharge-induced variations in mean flux reach the ecologically-important levels identified by these nutrient reduction goals. In general, large discharge-induced variations in flux may have biological consequences that limit the overall effectiveness of management controls. Moreover, discharge-related variations in flux contribute noise to measurement records, and will complicate the detection of changes in flux caused by nutrient control efforts.

Most of the monitoring stations show modest year-to-year variations in the annual estimates of flux (Figure 3). Although the CV values for all stations span about two orders of magnitude, ranging from 0.03 to about 3.0, values for most stations cover a narrower range from 0.21 to 0.41 (25th and 75th percentiles, respectively; median = 0.29). A majority of the stations also display relatively small annual EP values as indicated by a station median of 0.06. At about 60% of the stations, the annual probability of exceeding the long-term median annual flux by 50% is less than 0.10. For most stations, this suggest that the annual mean flux exceeds the long-term median flux by

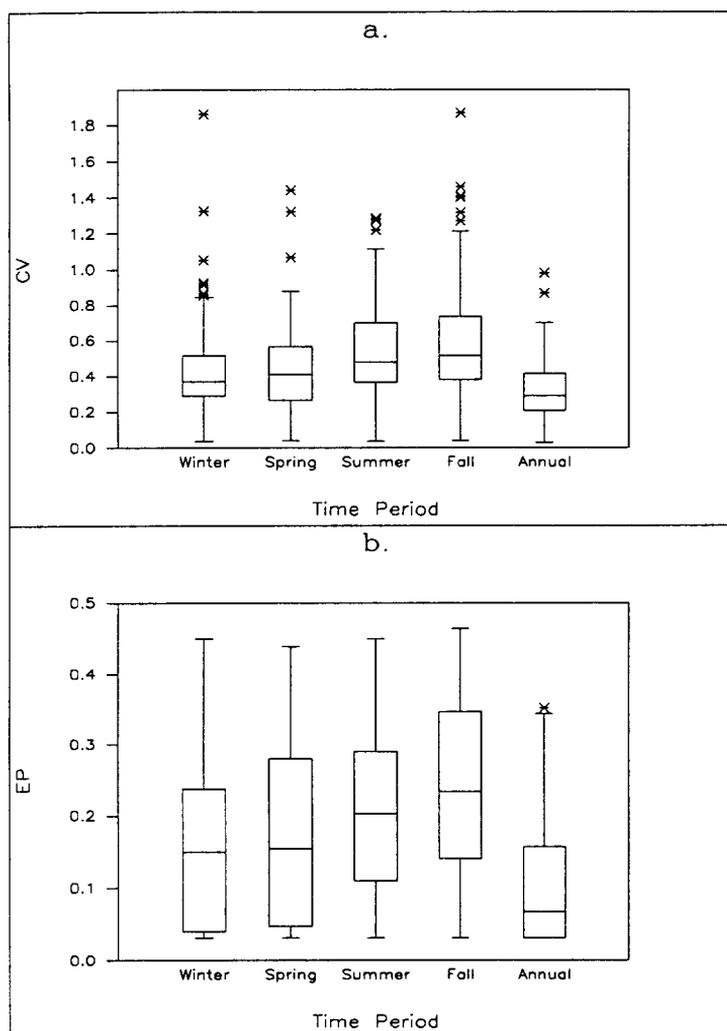


Figure 3. Distribution of (a) the CV and (b) the EP for seasonal and annual mean nitrate flux. Refer to the methods section for an explanation of the box and whisker plots. The maximum CV values for the seasonal and annual periods ranged from 3.3 to 3.7, and plot beyond the limits of the axis.

more than 50% in fewer than 10% of the years. At the remaining stations, the annual probability of exceedence ranges from 0.10 to a maximum of 0.35.

The seasonal estimates of flux display much greater year-to-year variability than is observed in the annual statistics. Values of both CV and EP are higher at more stations in each of the four seasons than comparable statistics based on annual flux. Based on comparisons of the medians of the station distributions

(Figure 3), the seasonal estimates of CV exceed comparable annual values by a magnitude of 1.3 to 1.8, whereas the seasonal EP estimates exceed annual values by an even larger magnitude of 2.5 to nearly 4.

The greatest variability in seasonal flux occurs during the low flow seasons of the year, the summer (median CV = 0.48, EP = 0.20) and fall (median CV = 0.52, EP = 0.23), as compared with the high flow seasons of the year, the winter (median CV = 0.37, EP = 0.15) and spring (median CV = 0.41, EP = 0.15). In general, the year-to-year variability in the winter and spring flux is commonly only about one third to one quarter as large as that observed in the summer and fall flux.

In conclusion, the magnitude of streamflow-induced variations in annual mean flux in Atlantic estuarine tributaries span a very wide range from 3–200% of the long-term mean flux, although variations more typically range from about 20–40% of the long-term mean. Annual exceedences of the long-term median annual flux by more than 50% occur infrequently at most stations (60% of stations with probabilities < 0.10) with more frequent exceedences of this flux level occurring at the remaining sites (40% of stations with probabilities of 0.10 to 0.35). Seasonal flux displays from about 1.5 to 4 times as much discharge-related variability as does annual flux. In general, the magnitude of variability in seasonal flux is inversely related to the size of the seasonal flux and discharge. That is, the largest variability in flux (large CV and EP values) occurs during the summer and fall, seasons with the smallest flux and discharge. The smallest variability in flux (small CV and EP values) occurs during the winter and spring, seasons with the largest flux and discharge. It is important to note that the small relative variability in flux during the winter and spring seasons (as indicated by the CV and EP statistics) is likely to be associated with large absolute variability in flux, and vice versa for the summer and fall seasons. Resource managers face the challenge of determining for individual estuaries and seasons the importance of these relative variations in flux to ecological resources and management goals.

Geography of annual and seasonal flux variability

Both the EP and CV statistics display very similar geographic patterns for the regions of the Atlantic. We describe the geography of flux variability only for the EP statistics in this paper.

The most distinct geographic pattern in annual and seasonal flux variability is the separation of the relatively large flux variability in the Western Gulf of Mexico region and Red River from the significantly smaller variability in all other major rivers and regions (Figure 4). The Western Gulf of Mexico rivers are generally characterized by large drainage areas and very small runoff.

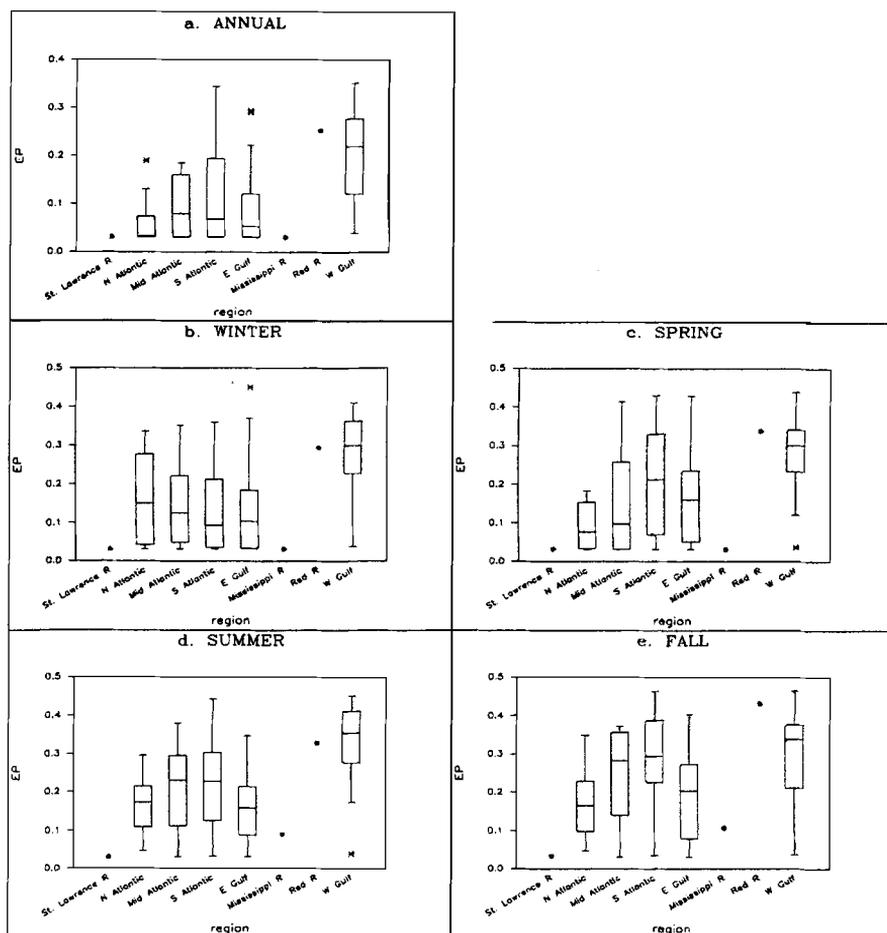


Figure 4. Distribution of the EP for (a) annual mean nitrate flux, and seasonal mean nitrate flux for (b) winter, (c) spring, (d) summer, and (e) fall by regional drainage divisions of the Atlantic coastal zone. Refer to the methods section for an explanation of the box and whisker plots. The solid points describe the flux statistics for the three largest rivers.

Many of these rivers experience storms throughout the year which produce flashy or highly variable discharge and flux conditions. The flux variability for these rivers as measured by the EP (Figure 4) is consistently large in all seasons of the year, although somewhat greater variability is evident in the summer and fall seasons. The probability of exceeding the seasonal median flux by 50% in the Western Gulf of Mexico rivers typically ranges from about 0.20 to 0.40.

Of the other major rivers and regions, the smallest variability in flux occurs in the St. Lawrence River, the Mississippi River, and the North Atlantic region, whereas the Mid Atlantic, South Atlantic, and Eastern Gulf of Mexico regions generally show somewhat larger variability in flux. In the nine monitored tributaries to the Chesapeake Bay (Mid Atlantic), the annual exceedence probability ranges from <0.03 to 0.18 of which the three largest rivers show annual EP estimates of <0.03 (Susquehanna R.), 0.10 (Potomac R.), and 0.10 (James R.). The Neuse River, a major tributary to the Pamlico Sound (South Atlantic), shows an annual exceedence probability of <0.03 .

The inverse relation between the magnitude of year-to-year variability in seasonal flux and the magnitude of seasonal flux and discharge, described in the previous section, is most evident in EP statistics for the Mississippi River and for rivers of the Mid Atlantic and South Atlantic regions (Figure 4). In these rivers, larger flux variability generally occurs in the summer and fall seasons, whereas smaller flux variability occurs in the winter and spring seasons. In the fall season, the Mid Atlantic and the South Atlantic regions display flux variability equally as large as that observed in the Western Gulf of Mexico region. Seasonal differences in flux variability in the Neuse River (EP = <0.03 , <0.03 , 0.24, and 0.41 for the winter, spring, summer, and fall seasons, respectively), a major Pamlico Sound tributary (South Atlantic), are consistent with this more generally observed seasonal pattern. This seasonal characteristic is also evident in the Chesapeake Bay tributaries (Mid Atlantic) where summer/fall EP estimates (medians of 0.26 and 0.35, respectively) routinely exceed those in the winter/spring (medians of 0.12 and 0.11, respectively) by a factor of two to three. However, the James River, the third largest tributary to the Bay, shows variability in spring flux (EP = 0.35) as large or larger than that observed during the summer (EP = 0.26) and fall (EP = 0.37) seasons.

The inverse seasonal relation is somewhat less evident in the North Atlantic where moderate flux variability occurs in the summer and fall seasons as well as the wet months of the winter season. In contrast to the general pattern, year-to-year variability in the seasonal mean flux of the St. Lawrence and the Eastern and Western Gulf of Mexico coastal rivers is of a similar magnitude in most seasons.

Relation of flux variability to watershed characteristics

In general, a variety of natural and cultural watershed characteristics govern the magnitude of temporal variations in nitrate flux, and could explain differences in flux variability from one river to another. These may include the type and magnitude of nutrient sources as well as numerous physical, chemical, and biological factors affecting the transport of nitrate in watersheds. As an

example of the effect of sources, nitrate flux would be expected to be relatively unresponsive to discharge variations in watersheds dominated by generally constant flux from municipal wastewater treatment plants and industries, whereas nitrate flux in watersheds dominated by agricultural and urban nutrients in runoff should display greater sensitivity to variations in flow. Factors affecting nitrate transport in watersheds may include, for example, climatic conditions as described by basin precipitation, evapotranspiration, and stream discharge as well as a variety of watershed characteristics such as reservoirs, terrestrial and aquatic vegetation, physical and chemical properties of soils, geology, and channel morphology. Our estimates of discharge-related flux variations including CV, EP, and flux elasticity incorporate the integrated effects of these various processes. To evaluate the possible influence of some of these processes, we describe geographic differences in flux variations in relation to several simple measures of the natural and cultural characteristics of the watersheds including mean annual runoff for the period of record, drainage area, land use (percent urbanization), and population density. Land use data for 1987 were obtained for counties of the United States from the National Resources Inventory (U.S. SCS 1989). Population data for 1980 were obtained from the U.S. Bureau of Census (1983). Estimates of the percent land use and population density of NASQAN basins were computed by intersecting the drainage basin boundaries with counties and census-unit centroids using a geographic information system. County land-use data were aggregated by watershed in proportion to the area shared in common.

The geographic differences in flux variability as measured by the CV and EP statistics are most strongly related to the runoff conditions and type of nutrient sources in the watersheds. These relations are equally significant for seasonal and annual values. Moderately high, statistically significant negative Spearman's Rho correlations (S_p) exist between the percent urbanization of the watershed and the station values of CV and EP [S_p ranges from -0.23 ($p = 0.02$) to -0.39 ($p < 0.0001$) for various seasonal and annual values]. Correlations of seasonal and annual CV and EP values with the population density of the watersheds are also negative and statistically significant, ranging from -0.17 ($p = 0.09$) to -0.31 ($p = 0.002$). Significant, negative correlations ranging from -0.25 ($p = 0.01$) to -0.52 ($p < 0.0001$) exist between seasonal and annual values of CV and EP and the mean watershed runoff. Drainage basin size was not statistically related to the estimates of CV and EP. In sum, the magnitude of variability in flux generally increases with the quantity of nonurban land use and the extent of arid conditions in the watershed.

Although simple measures of several hydrologic and cultural characteristics of the watersheds are related to the magnitude of nitrate flux variations,

considerable unexplained geographic differences exist in the estimates of flux variability. These differences could possibly be explained by a more rigorous investigation of various measures of the hydrologic and chemical response of watersheds including soil characteristics, terrestrial and stream morphology, basin vegetation, types of nutrient sources, and storm path, frequency, and duration. The role of reservoirs in regulating the variability of flux and flow may also be significant in view of the large number of impoundments on coastal rivers of the North Atlantic.

Elasticity of annual and seasonal flux

In contrast to the previous descriptions of the historical variability in flux, this section quantifies the relative sensitivity of flux to changes in streamflow. Adopting terminology from the economic literature, we define flux sensitivity in terms of elasticity, or the percentage increase in flux associated with a one percent increase in streamflow. Elasticity estimates satisfy two general needs for information on the change in flux to expect from hypothetical changes in streamflow. First, in the absence of nutrient monitoring records, flux elasticity estimates allow for approximation of flux variability in regions where the variability of streamflow is only generally known. Second, the elasticity values, combined with available climatic and hydrologic data, provide approximate estimates of the effects of future climatically-induced changes in streamflow on nutrient flux.

Figure 5 displays the station distributions of flux elasticity by region based on a 1% increase in mean annual discharge. Flux elasticities range from 0.05% to 1.59%. For most stations ("all regions" in Figure 5), the predicted change in nitrate flux is slightly less than unity (median = 0.93%) with estimates commonly varying from 0.69% to 1.12%, the 25th and 75th percentiles, respectively. Elasticities of one or larger are strongly indicative of rivers where runoff, either from agricultural, urban, or forested lands, is the predominant source of river nitrate. Moreover, elasticities greater than unity potentially describe more challenging management situations because of the disproportionate effect of streamflow changes on flux in these watersheds.

Some modest differences in flux elasticities are visible among the various coastal regions (see Figure 5). The streams of the Eastern Gulf of Mexico tend to show the smallest elasticities (median = 0.78%), whereas the streams of the Atlantic (medians ranging from 0.94% to 0.98%) and Western Gulf of Mexico (median = 1.16%) regions show the largest estimates. By comparison to other regions, the rivers of the Western Gulf of Mexico show the widest range in flux elasticities.

The geographic distribution of flux elasticity is generally similar to that observed for the measures of historical flux variability (EP and CV). In

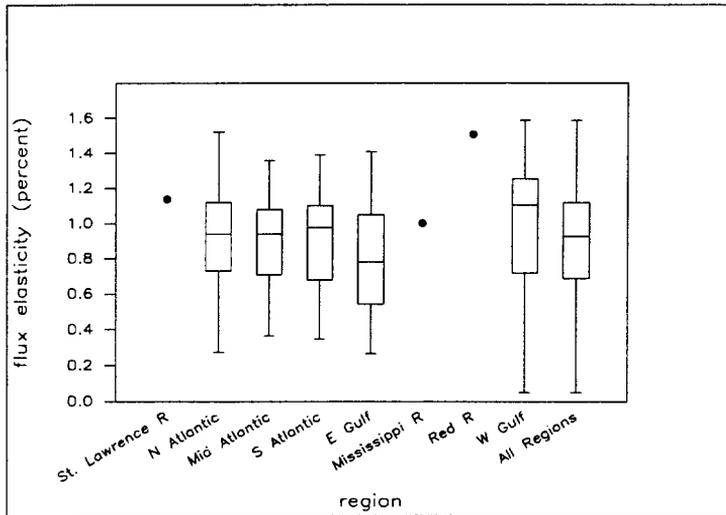


Figure 5. Distribution of nitrate flux elasticity by regional drainage divisions of the Atlantic coastal zone. Refer to the methods section for an explanation of the box and whisker plots. The solid points describe the flux statistics for the three largest rivers.

fact, flux elasticity is highly correlated with both the EP ($S_p = 0.59$) and CV ($S_p = 0.72$) statistics. Similar natural and cultural basin characteristics are also of importance in explaining the geographic distribution of flux elasticity. Elasticity is negatively correlated with mean basin runoff ($S_p = -0.20$; $p = 0.047$) and measures of point sources [i.e., population density ($S_p = -0.21$; $p = 0.038$) and urban land area ($S_p = -0.32$; $p = 0.001$)]. Whereas earlier relations of flux variability to drainage basin size were insignificant, flux elasticity is positively correlated with basin area ($S_p = 0.22$; $p = 0.029$). This relation is readily apparent for the three largest rivers, the St. Lawrence, Mississippi, and Red, which show among the largest flux elasticities (1.14, 1.00, and 1.51, respectively). Despite their historically small relative variability in streamflow and flux, these rivers demonstrate a comparatively large potential for changes in flux in response to future changes in discharge. In sum, the findings suggest that the sensitivity of flux to changes in discharge generally increases with the size of the watershed, the percentage of the watershed in nonurban land use, and the extent of arid climatic conditions.

The estimates of flux elasticity corresponding to changes in mean annual streamflow sufficiently describe changes in flux over a relatively wide range of discharge conditions. At each station, we computed estimates of flux elasticity for a 1% increase in the seasonal mean discharge. The largest mean flows

occur during the winter/spring seasons, exceeding those of the summer/fall seasons by 50 to 200%. The seasonal estimates of flux elasticity are virtually identical to one another, and are very similar to the annual estimates. Despite the existence of some curvature in the flux-discharge relations (the quadratic discharge term in equation 2 was selected for about 60% of the stations), the similarities in flux elasticity suggest that the linear discharge term has a predominant effect over the relatively wide range of seasonal mean flows.

The use of estimates of flux elasticity to address questions of the possible effects of global warming on nutrient fluxes must await improvements in our understanding of the linkages between global warming and changes in climate and hydrology. Large uncertainties exist in global climate model predictions of the direction, magnitude, and frequency of temperature, evaporation, and precipitation changes, particularly at the regional scale. Current predictions of changes in precipitation associated with a doubling of CO₂, for example, display wide disparity in magnitude for the United States (Lins et al. 1990).

Hydrologic models linking changes in precipitation and evapotranspiration to changes in runoff conditions may entail somewhat less uncertainty. One simulation (Schaake 1990) for the southeastern quadrant of the United States based on a water balance model predicts runoff elasticities in terms of streamflow changes relative to changes in precipitation and evapotranspiration. Runoff elasticities range from about 2 to 4.5, increasing in magnitude from the moist eastern to the arid western portions of the quadrant. Thus, the elasticities of nitrate flux with respect to precipitation in arid regions of the United States may reach 5.0 or more (i.e., 1.2×4.5).

Case studies of extreme variations in nitrate flux

The 15- to 20-year records of nitrate and streamflow analyzed in the previous sections are adequate to characterize the seasonal and annual variability of nitrate flux for recurrence intervals as large as a few tens of years. Due to the limitations of available data, however, the statistical reliability of these flux estimates under higher streamflow conditions (i.e., larger recurrence intervals) may be greatly reduced. Nevertheless, information on the potential for more extreme flux levels under streamflow conditions with longer recurrence intervals is of interest to managers.

In this section, we supplement the statistical analyses of the previous sections using limited data from investigations of three unusual meteorological events. Our objectives are twofold. First, we use the initial two case studies to determine whether estimates of nitrate flux under unusually high streamflow conditions differs greatly from estimates based on our previous analyses. Second, we use each of the case studies to illustrate the significant contri-

Table 2. Mean nitrate-nitrogen flux from the Mississippi River to the Gulf of Mexico during flood conditions (July–September, 1993) and during more normal conditions (July–September, 1991/92). Data are from Goolsby, 1994.

Year	Water flux (meters ³ /sec)	Nitrate flux [#] (metric tons/day)
1991	9,800	1,400
1992	14,300	1,830
1993	26,700	4,350

[#] Flux estimates are based on 19, 12, and 34 concentration observations for the years 1991, 1992, and 1993, respectively.

butions of elevated nitrate flux to the widespread ecological disturbances associated with unusual meteorological events. The three case studies include the response of the lower Mississippi River to an extended period of rain in the midwestern U.S. during the summer of 1993, the effects of Tropical Storm Agnes on the Susquehanna River and Chesapeake Bay in the summer of 1972, and the effects of a set of unusual meteorological and estuarine conditions in the Baltic Sea in 1988.

Mississippi River flood of 1993

Sustained, torrential rains in the upper portions of the midwestern United States during the summer of 1993 produced flood conditions in the lower Missouri and central Mississippi River Basins equaling or exceeding the 100-year recurrence interval (Dowgiallo 1994). The results of a large number of investigations of the effects of the flooding were published by the U.S. Department of Commerce (Dowgiallo 1994). Measurements of streamflow and nitrate flux in the lower Mississippi River during the July to September months of 1993 reflect larger than normal flows entering the Gulf of Mexico. These measurements are compared in Table 2 to those taken in the same months of 1991 and 1992 under more normal conditions. According to these data, streamflow in the lower Mississippi River approximately doubled during the summer of 1993 (increasing by a factor of 1.9 and 2.7 over 1991 and 1992 levels, respectively), and nitrate flux showed a nearly proportional rise, increasing by a factor of 2.4 and 3.1, respectively. Annual exceedences of more than 1.5 times the long-term median summer flux would be expected to occur with a probability of 0.09 based on seasonal EP statistics for the Mississippi River.

We compared the 65 instantaneous samples collected from July to September of 1991–93 (Table 2) with the previously analyzed data for years

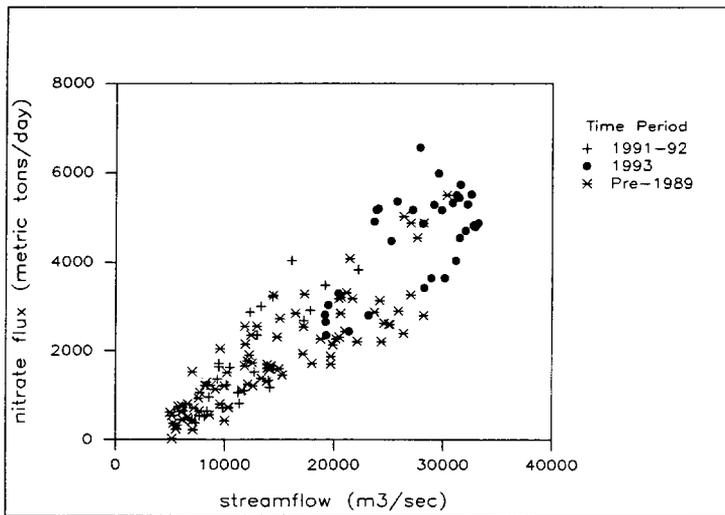


Figure 6. Nitrate flux and streamflow for the Mississippi River at Baton Rouge, Louisiana. Measurements for the pre-1989 period were collected in the NASQAN program. Measurements for 1991–93 are from D.A. Goolsby, U.S. Geological Survey, written communication, 1995.

prior to 1989 to assess any differences in the flux-discharge relation. Although the higher streamflows for 1993 moderately expand the range of sampled flows, the flux-discharge relation remains virtually unchanged as the 1993 high-flow data and the 1991–92 “normal-year” data are entirely consistent with the previously analyzed data (Figure 6). As additional confirmation, we separately fit a flux-discharge regression model to the 1991–93 data ($R^2 = 0.83$), and estimated a flux elasticity of 1.1. This elasticity value indicates that a 1.1% increase in nitrate flux is expected for each 1% increase in streamflow. This elasticity estimate is practically identical to our earlier estimate of 1.0 for the Mississippi River based on the pre-1989 NASQAN data (Figure 5). These near-unity estimates indicate the approximate linearity of the flux-discharge relation over a very wide range of streamflows including the higher flows associated with the extreme meteorological event of 1993.

Elevated levels of nitrate flux in the summer of 1993 contributed to a nearly 15-fold increase in total phytoplankton over 1990–92 levels on the Louisiana shelf (Dortch 1994). Species composition underwent large changes with cyanobacteria and diatoms accounting for much of the phytoplankton increases. Diatom growth was significantly enhanced by the increased availability of silicate (Dortch 1994). The changes in phytoplankton growth extended the normal summer-time oxygen depletion of coastal shelf bottom waters well into the fall of 1993 (Rabalais et al. 1994). The zone of oxygen

depletion (i.e., the “dead zone”) also became much more widespread during the summer flood conditions of 1993 than observed during the previous eight years as hypoxic conditions extended over much greater distances offshore and parallel to the Louisiana shore (Rabalais et al. 1994).

Tropical Storm Agnes flood of 1972

Tropical Storm Agnes produced floods with estimated recurrence intervals of about 100 to 200 years on most major tributaries to the Chesapeake Bay in June, 1972. The water volume entering the Bay during this one month represented approximately half the mean low water volume of the Bay (Smith et al. 1977). The results of extensive investigations of the effects of the storm were published by The Chesapeake Research Consortium, Inc. (1977).

Measurements of streamflow and nutrient concentrations (see Table 3) for the Susquehanna River, the largest tributary to the Chesapeake Bay, were made during a twelve-week period surrounding the storm (Schubel et al. 1977). For a one week period following the storm’s peak on June 21, average streamflow exceeded the normal average June streamflow by a factor of nearly 20 (The Chesapeake Research Consortium, Inc. 1977). Streamflows rapidly returned to normal levels within about one month following the Agnes storm. Unfortunately, measurements of nitrate concentration were available only for a single pre-storm period and during the recession of the flood, beginning 20 days after the storm peak. Comparisons of pre-storm concentrations with the July post-storm concentrations show an increase by nearly a factor of two. Using the available data (Table 3), we fit a flux-discharge regression model ($R^2 = 0.92$), and estimated a flux elasticity of 1.1. This elasticity estimate is nearly identical to the earlier model estimate of 0.98 based on NASQAN measurements for the Susquehanna River (Figure 5). These near-unity estimates provide evidence of an approximately linear flux-discharge relation over the sampled range of streamflows including the moderately high flows observed immediately after the Agnes storm.

It is important to note that measurements of the Agnes flood provide only limited insight into the statistical reliability of our flux estimates under more extreme flow conditions. A major limitation is the lack of concentration, and thus, flux measurements during the peak of the storm when discharge, and presumably flux, changed abruptly. During this period, streamflow exceeded the largest recorded NASQAN flow of 12,800 m³/sec by nearly a factor of 2.5. Moreover, flux measurements made during the recession period (July through September of 1972) corresponded to streamflows that were no larger than the 60th percentile of the recorded NASQAN flows. Therefore, the Agnes storm data provided only marginal improvement in our knowledge of the response of nitrate flux to more extreme streamflows in the Susquehanna River.

Table 3. Changes in inorganic nitrate+nitrite-nitrogen flux from the Susquehanna River to the Chesapeake Bay during an twelve-week period surrounding the Tropical Storm Agnes (based on concentration data from Schubel and others, 1977[#] and U.S. Geological Survey streamflow records for the Susquehanna River at Conowingo, Maryland).

Date (1972)	Streamflow (m ³ /sec)	Concentration (mg/L-N)	Flux (metric tons/day)
12-16 June	969	0.53	45
24 June	31,700*	—	—
13 July	1,800	0.83	128
20-22 July	1,210	1.04	108
3-5 August	445	0.81	31
15-17 August	493	0.74	32
28-31 August	374	0.62	20
16-18 September	87	0.39	3

[#] Concentration data are from Chesapeake Bay sampling locations within 30 to 80 kilometers of the mouth of the Susquehanna River.

* This peak streamflow occurred three days after the peak of Agnes precipitation.

Numerous ecological disturbances resulted from the storm including reductions in the biomass of shellfish and submerged aquatic vegetation due to changes in turbidity, temperature, salinity, and in some cases dissolved oxygen. Elevated nutrient flux led to the rapid growth of phytoplankton in the months immediately following the flood and continuing through the fall of 1972. The flood significantly altered both the species composition and seasonality of algal blooms, effects which persisted into 1973 (Zubkoff & Warinner 1977). Abnormally large blooms occurred at the mouth of the Bay in the summer, one year following Agnes, as accumulated nutrients were released from benthic sediments. These increases in algal growth in 1972 and 1973 contributed to more widespread occurrences of dissolved oxygen deficits than had been previously observed in the Bay and its tributaries (Schubel & Cronin 1977; Jordan 1977). Although Agnes caused significant ecological damages, the Chesapeake Research Consortium (1977) concluded that the Chesapeake Bay ecosystem displayed great resiliency as recovery occurred over a period of a few years.

Baltic Sea

The final case study illustrates one of the more complicated scenarios facing coastal resource managers; the simultaneous occurrence of events that separately are benign, but in combination, create toxic conditions. In May of 1988, a combination of natural and man-made events caused unusually large blooms of *Chrysochromulina polylepis*, a toxin-producing flagellate,

leading to massive fish kills in the narrows connecting the North and Baltic Seas (Rosenberg et al. 1988). Over the decade of the 1980s, nitrogen flux to the region increased by a factor of 4 to 6, and both algal blooms and fish kills occurred in association with seasonally-elevated nitrogen concentrations. During the winter of 1987–88, nutrient flux to the region was 80% higher than the 10-year mean, and water temperatures in the Baltic Sea were 2 degrees warmer than normal. By late spring, nitrogen concentrations in surface waters of the region are typically depleted as a result of biological uptake during the spring bloom. However, the high nitrogen flux during the early spring of 1988 exceeded the nutrient requirements of the phytoplankton, leaving residual nitrogen available for algal growth in the late spring. The resulting blooms were attributable to a unique combination of lingering nitrate concentrations from the spring freshet, sunny days, and persistent easterly winds that reduced mixing, allowing surface-water temperatures to rise quickly (Rosenberg et al. 1988). Nitrogen concentrations during this catastrophic bloom were much lower than the concentrations present during the less-problematic bloom of two months earlier.

Case study conclusions

The available data from the first two case studies tend to confirm the statistical reliability of our flux estimates under more extreme streamflow conditions in two large river systems, although the second study of tropical storm Agnes did not actually extend the range of sampled streamflows beyond that of the NASQAN record for the Susquehanna River. The above-normal increases in nitrate flux and streamflow documented by the first two case studies produced flux elasticity estimates nearly identical to those from our previous analyses of generally lower streamflow conditions. These near-unity elasticity estimates indicate an approximately linear flux-discharge relation over a very wide range of flows in these rivers. Unfortunately, the case studies do not provide an opportunity to examine and evaluate flux responses to extremely high streamflows in watersheds with nonlinear flux-discharge relations and flux elasticities above one. Although many of the NASQAN coastal rivers display a disproportionate flux response (elasticity above one), we are unable to provide managers with information on the potential for disproportionately high levels of nitrate flux from these watersheds during the largest, most infrequent storms.

All three case studies demonstrate that increased nitrate flux may contribute significantly to the ecological disturbance caused by extreme meteorological events. In some estuaries, especially those where tributaries exhibit nitrate flux elasticities well above unity, concern over the potentially severe consequences of increased nutrient flux could prompt the use of additional

nutrient controls during certain seasons of the year. Management plans need to consider the potential response of individual estuarine ecosystems to these unusual meteorological events.

Conclusions

Streamflow-related variability in nutrient flux represents an important source of uncertainty in managing coastal ecosystems. Quantification of flux variability is an important step towards characterizing the uncertainty facing coastal resource managers in adopting effective nutrient-reduction goals and monitoring progress towards these goals. Historical records of streamflow and water quality measurements for 104 USGS river monitoring stations permit an analysis of variability in annual and seasonal flux of nitrate to the Atlantic coastal zone.

Some general characteristics of streamflow-induced variability in nitrate flux emerge from the findings for tributaries to northwestern Atlantic estuaries. The magnitude of flux variability spans a very wide range and depends importantly upon the season of year and the climatic and land-use characteristics of the tributary watersheds. Year-to-year variations (CV statistic) in annual mean flux range over two orders of magnitude, from 3–200% of the long-term mean flux, although variations more typically range from 20–40% of the long-term mean. Annual exceedences of the long-term median annual flux by more than 50% (EP statistic) occur infrequently in most rivers (probability < 0.10) although more frequent exceedences of this level (probability = 0.10 to 0.35) are observed in 40% of the rivers. In tributaries to two major northwestern Atlantic estuaries (the Chesapeake Bay and Pamlico Sound) where this exceedence level has particular management relevance, exceedences of the long-term median annual flux by more than 50% typically occur in fewer than 10% of the years, although exceedences of the long-term median seasonal flux by more than 50% can occur with much higher frequency. For most of the regions, streamflow-induced variability in seasonal flux is from 1.5 to 4 times as large as the variability in annual flux. In Atlantic coastal rivers, the summer and fall seasons display the largest relative variability, with less relative variability occurring in the winter and spring seasons. However, because the winter and spring seasons account for about 70% of the nitrate exported annually, the smaller relative variability in flux during these seasons may have ecologically-important implications for estuaries. The western Gulf of Mexico estuaries, where nitrate fluxes are both highly elastic and highly variable in all seasons, may present one of the most challenging environments for managing nutrient inputs. More generally,

managers must contend with larger flux variability in more arid watersheds and in watersheds dominated by nonpoint sources of nitrogen.

Although these characteristics provide a general framework for initially discussing management goals, resource managers must ultimately address the difficulties imposed by temporal variability in flux for individual estuaries. Ideally, management goals need to account for streamflow-related variations in mean flux that have important ecological effects. The use of additional nutrient controls to address the effects of seasonal and annual variations in mean conditions will generally depend on managers' assessments of the likelihood of large flux variations, the size of the flux response to streamflow variations, the importance of nutrient variability to the health of estuarine ecosystems, and the costs of added controls. The findings presented in this paper primarily provide insight into the first two topics, although the EP statistics have bearing on the third issue of estuarine health for at least two major northwestern Atlantic estuaries. In future analyses, measures of historical variations in flux, such as the EP statistic, could be adjusted to improve managers' understanding of the likelihood of ecologically-relevant natural variations in flux for particular estuaries. Also, in tracking the progress of control efforts, the flux-discharge models presented in this paper incorporate flux variability, and thus provide the statistical framework for future determinations of the appropriate number of samples and length of time required to detect management-related changes in the nutrient flux of fluvial systems.

Large, infrequent meteorological events present a unique challenge for managing coastal ecosystems due to their extreme uncertainty coupled with significant ecological consequences. Data from the case studies provided limited evidence confirming the statistical reliability of our flux estimates under the more extreme streamflow conditions associated with these unusual events. These case studies provided examples of nearly proportional increases in seasonal streamflow and flux over a wide range of flows. These studies also illustrated that nutrient flux plays an important, but complementary role in the far-reaching effects of unusual meteorological events on estuarine processes. Nevertheless, the potentially severe effects of these events in some estuaries may provide added incentive for adopting lower limits on nutrient fluxes. Although the validity of the flux models is less certain for extreme meteorological events, our results suggest that the highly elastic nitrate flux of large, nonurban watersheds may exhibit the most pronounced response to unusual storms.

References

- Bradu D & Mundlak Y (1970) Estimation in lognormal linear models. *J. Am. Stat. Assoc.* 65: 198–211
- Brockmann UH & Eberlein K (1986) River input of nutrients into the German Bight. In: Skreslet S (Ed) *The Role of Freshwater Outflow in Coastal Marine Ecosystems* (pp 231–240). Springer-Verlag, New York
- Chesapeake Research Consortium, Inc. (1977) *The effects of Tropical Storm Agnes on the Chesapeake Bay estuarine system.* CRC Publication No. 54. The Johns Hopkins University Press, Baltimore, Maryland
- Cohn TA, Caulder DL, Gilroy EJ, Zynjuk LD & Summers RM (1992) The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay. *Water Resour. Res.* 28: 2353–2363
- Cohn TA, DeLong LL, Gilroy EJ, Hirsch RM & Wells DK (1989) Estimating constituent loads. *Water Resour. Res.* 25: 937–942
- Cunnane C (1978) Unbiased plotting positions: A review. *J. Hydrol.* 37: 205–222
- Dortch Q (1994) Changes in phytoplankton numbers and species composition. In: Dowgiallo M (Ed) *Coastal Oceanographic Effects of Summer 1993 Mississippi River Flooding* (pp 46–49). National Oceanic and Atmospheric Administration Special Report, Washington DC
- Dowgiallo M (Ed) (1994) *Coastal Oceanographic Effects of Summer 1993 Mississippi River Flooding.* National Oceanic and Atmospheric Administration Special Report, Washington, DC
- Ferguson RI (1986) River loads underestimated by rating curves. *Water Resour. Res.* 22: 74–76
- Fransz HG (1986) Effects of fresh water inflow on the distribution, composition and production of plankton in the Dutch coastal waters of the North Sea. In: Skreslet S (Ed) *The Role of Freshwater Outflow in Coastal Marine Ecosystems* (pp 241–249). Springer-Verlag, New York
- Gilroy EJ, Hirsch RM & Cohn TA (1990) Mean square error of regression-based constituent transport estimates. *Water Resour. Res.* 26: 2069–2077
- Goolsby DA (1994) Flux of herbicides and nitrate from the Mississippi River to the Gulf of Mexico. In: Dowgiallo M (Ed) *Coastal Oceanographic Effects of Summer 1993 Mississippi River Flooding* (pp 32–35). National Oceanic and Atmospheric Administration Special Report, Washington DC
- Hirsch RM (1982) A comparison of four record extension techniques. *Water Resour. Res.* 15: 1781–1790
- Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T, Berendse F, Freney J, Kudryarov V, Murdoch P & Zhao-liang Z (1996) Regional Nitrogen Budgets and Riverine Nitrogen Fluxes for the Drainage Systems of the North Atlantic Ocean: Natural and Human Influences. *Biogeochemistry*, in press
- Jordan RA (1977) Observations of dissolved oxygen conditions in three Virginia estuaries after Tropical Storm Agnes (Summer, 1972). In: The Chesapeake Research Consortium, Inc. (Eds) *The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System* (pp 348–367). CRC Publication No. 54. The Johns Hopkins University Press, Baltimore Maryland
- Koch RW & Smillie GM (1986) Bias in hydrologic prediction using log-transformed regression models. *Water Resour. Bul.* 22: 717–723
- Langford RH & Kapinos FP (1979) The national water data network: A case history. *Water Resour. Res.* 15: 1687–1691
- Lins HF, Hare RK & Singh KP (1990) Influence of the atmosphere. In: Wolman MG & Riggs HC (Eds) *The Geology of North America Volume O-1: Surface Water Hydrology* (pp 11–53). The Geological Society of America Inc., Boulder, Colorado
- Loucks DP, Stedinger JR & Haith DA (1981) *Water Resource Systems Planning and Analysis.* Prentice Hall Inc., Englewood Cliffs, New Jersey

- Montgomery DC & Peck EA (1982) Introduction to Linear Regression Analysis. John Wiley and Sons, New York
- Paerl HW (1987) Dynamics of blue-green algal (*Microcystis aeruginosa*) blooms in the lower Neuse River, North Carolina: causative factors and potential controls. Institute of Marine Sciences, University of North Carolina, UNC-WRRI-87-229, Morehead City, North Carolina
- Queguiner B & Treguer P (1986) Freshwater outflow effects in a coastal, macrotidal ecosystem as revealed by hydrological, chemical and biological variabilities (Bay of Brest, Western Europe). In: Skreslet S (Ed) The Role of Freshwater Outflow in Coastal Marine Ecosystems (pp 219–230). Springer-Verlag, New York
- Rabalais NN, Turner RE & Wiseman WJ (1994) Hypoxic conditions in bottom waters on the Louisiana-Texas shelf. In: Dowgiallo M (Ed) Coastal Oceanographic Effects of Summer 1993 Mississippi River Flooding (pp 50–54). National Oceanic and Atmospheric Administration Special Report, Washington DC
- Rosenberg R, Lindahl O & Blank H (1988) Silent spring in the sea. *Ambio*. 17: 289–290
- Salati E, Sylvester-Bradley R & Victoria RL (1982) Regional gains and losses of nitrogen in the Amazon basin. *Plant and Soil* 67: 367–376
- Schaake JC (1990) From climate to flow. In: Waggoner PE (Ed) Climate Change and the Planning and Management of U.S. Water Resources (pp 177–206). Report to the American Assoc. for the Advancement of Science Panel on Climatic Variability. John Wiley and Sons, New York
- Schubel JR & Cronin WB (1977) Effects of Agnes on the distribution of dissolved oxygen along the main axis of the Bay. In: The Chesapeake Research Consortium, Inc. (Eds) The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System (pp 335–347). CRC Publication No. 54. The Johns Hopkins University Press, Baltimore, Maryland
- Schubel JR, Taylor WR, Grant VE, Cronin WB & Glendening M (1977) Effects of Agnes on the distribution of nutrients in Upper Chesapeake Bay. In: The Chesapeake Research Consortium, Inc. (Eds) The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System (pp 311–319). CRC Publication No. 54. The Johns Hopkins University Press, Baltimore, Maryland
- Smith CL, MacIntyre WG, Lake CA & Windsor JG (1977) Effects of Tropical Storm Agnes on nutrient flux and distribution in Lower Chesapeake Bay. In: The Chesapeake Research Consortium, Inc. (Eds) The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System (pp 299–310). CRC Publication No. 54. The Johns Hopkins University Press, Baltimore, Maryland
- Taylor R (1984) The runoff of nitrogen and phosphorus compounds from selected agricultural regions in the Vistula and Odra drainage basins. *Oceanologia* 18: 135–147
- Thomann RV, Collier JR, Butt A, Casman E & Linker LC (1994) Technical analysis of response of Chesapeake Bay water quality model to loading scenarios. A report of the modeling subcommittee. Chesapeake Bay Program Office. Annapolis Maryland CBP/TRS 101/94
- Tukey JW (1977) Exploratory Data Analysis. Addison-Wesley Pub., Reading, MA
- US Bureau of Census (1983) Census of population and housing 1980: Master area reference file (MARF) 2 [machine-readable datafile]. Washington DC
- US Soil Conservation Service (1989) Summary report 1987 – National resources inventory. US Soil Conservation Service Statistical Bulletin no. 790
- Zubkoff PL & Warinner JE (1977) The effect of Tropical Storm Agnes as reflected in Chlorophyll a and heterotrophic potential of the Lower Chesapeake Bay. In: The Chesapeake Research Consortium, Inc. (Eds) The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System (pp 368–339). CRC Publication No. 54. The Johns Hopkins University Press, Baltimore, Maryland