Water discharge, nitrate concentration and nitrate flux in the lower Mississippi River

S.P. Dinnel * and A. Bratkovich b

* Center for Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529, USA
b NOAA Great Lakes Environmental Research Laboratory, 2205 Commonwealth Blvd., Ann Arbor, MI 48105, USA

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ABSTRACT

Thirty-five years of monthly lower Mississippi River water discharge, nitrate concentration and nitrate flux have been analyzed. The potential predictability of these quantities has been evaluated. Results indicate a large amplitude, long-term cycle in the nitrate concentration that is not observed in the water discharge. A decrease in average nitrate concentration from a peak in 1983 to the present confirms that this variability is more cyclic than trend-like. River-water discharge variation was greatest in association with the annual cycle. The annual water discharge and nitrate concentration cycles were similar; high nitrate concentrations usually occurred near the vernal freshet, and low concentrations usually occurred along with autumnal low-flow conditions. Nitrate flux variations exhibited a low amplitude, long-term modulation of a dominant, annual cycle. A predictor-hindcast analysis indicates that truly skilled forecasts of all three fields are feasible.

Introduction

The Mississippi River system drains approximately 41% of the contiguous United States (Fig. 1), with an average water discharge that ranks first in North America and seventh in the world (van der Leeden et al., 1990). The Mississippi River is unusual in that it has two main distributaries. Over two thirds of the total flow discharges from the Mississippi River via the modern “Birdsfoot” Delta, and the rest discharges via the Atchafalaya River 250 km to the west (Dinnel and Wiseman, 1986). Not only does the Mississippi River discharge affect the water mass properties and the circulation in both the northeastern and northwestern Gulf of Mexico (Cochrane and Kelly, 1986; Dinnel and Wiseman, 1986; Dinnel, 1988), but the influx of nutrients impacts the ecology by increasing the primary production of coastal waters in the northern Gulf of Mexico (Gunter, 1963; Lohrenz et al., 1990; Dagg et al., 1991; Turner and Rabalais, 1991). Dissolved inorganic nitrogen is comprised of nitrate (NO₃⁻), ammonium (NH₄⁺) and nitrite (NO₂⁻), with nitrate having much larger concentrations than the other forms (Meybeck, 1982).

One prominent impact of riverine freshwater discharge is the significant increase in water column stability for the entire shelf region west of the Delta. The strong upper water column density stratification tends to inhibit the vertical fluxes of mass, momentum, energy and various constituents such as dissolved oxygen and nutrients.

The generation and maintenance of hypoxic shelf waters west of the Mississippi River Delta is one manifestation of the interplay between enhanced density stratification and elevated nutrient input levels associated with riverine fluxes. The exact sequence of physical–biological coupling mechanisms leading to shelf hypoxia has yet to be resolved. The NOAA-funded Nutrient Enhanced Coastal Ocean Productivity (NECOP) Program was recently initiated to study the overall ecosystem dynamics leading to shelf hypoxia in this region.
Any system analysis requires detailed characterizations of the various forcing and response functions considered potentially important to the integral operation of the system. As is typical of most ecological problems, the associated state variable fields have been observed or analyzed in limited spatial, temporal or topical contexts. However, there are few "off-the-shelf" functional representations of state variable fields other than land-based meteorological fields (which are routinely observed and analyzed by NOAA's National Weather Service). This work attempts to formulate quantitative descriptions of three of the most important forcing functions associated with the shelf hypoxia problem: riverine freshwater discharge (i.e. buoyancy flux), riverine nitrate concentration and riverine nitrate flux. If the above forcing functions are difficult to describe, quantify or predict at their source (before other processes intermediate), then the ultimate goals of quantifying, modeling or predicting shelf hypoxia events are probably unattainable.

Nitrate concentration in the lower Mississippi River has increased by a factor of two over the last 35 to 40 years (Walsh et al., 1981; Turner and Rabalais, 1991). Similar increasing trends in ni-
Water discharge, nitrate concentration and nitrate flux have been noted in other major rivers of the world and are considered to be anthropogenic, caused mainly by increased use of agricultural fertilizers and increased industrial and domestic wastes (Meybeck, 1982; GESAMP, 1987). Information from the latter half of the 1970's indicates an increasing nitrate concentration trend in many U.S. rivers. These increases were strongly associated with agricultural activity (not simply fertilizer use) and with atmospheric deposition, especially in the Ohio and upper Mississippi River drainage basins (Smith et al., 1987).

The ecological impacts of the increased nitrate concentrations to the coastal waters of the northern Gulf of Mexico are changing primary production characteristics (Lohrenz et al., 1990), possible association with near-bottom, low dissolved oxygen regions (Turner et al., 1987), and species succession due to changes in nutrient levels (Turner and Rabalais, 1991).

Monthly (one data value per month) nitrate concentration values progress through an annual cycle with high values in the spring and low values in the fall. This annual cycle is similar to the characteristic annual Mississippi River water discharge cycle. This similarity suggests that there is a significant relationship that could be used to "predict" nitrate flux from persistent patterns in water discharge and nitrate concentration variability.

In this work we examine the relationship of water discharge and nitrate concentration over a 35-year time period using linear correlation and time series analyses. We also examine the potential predictability of nitrate flux, nitrate concentration and fresh water discharge (buoyancy flux) using linear optimal estimator analysis.

Data and methods

Lower Mississippi River nitrate concentration data were extracted from U.S. Geological Survey (USGS) Surface Water Quality Reports for St. Francisville, LA (U.S. Department of the Interior, 1964–1990), with earlier data from Walsh et al. (1981). Data began in 1954 and continued through the 1989 water year. St. Francisville is approximately 450 km upstream from the Mississippi River Delta. Tarbert Landing, MS, 480 km upstream from the Mississippi River Delta was used for Mississippi River water discharge data (U.S. Army, 1954–1990). There are no major tributaries downstream of this gauging station on the Mississippi River.

Water discharge data were monthly averages of daily values and hereafter will be referred to as monthly water discharge. The nitrate concentrations used were "instantaneous" values sampled at approximately monthly intervals. The sampling procedure and methodology changed over the course of the record length. Before 1973 the nitrate concentration value at St. Francisville was determined as an average of multiple surface samples; after 1973 nitrate concentrations were determined as cross-sectional averages, using at least three vertical profiles. Before 1975 water samples were chilled, then analyzed; after 1975 water samples were preserved with mercuric chloride and chilled before analysis (C. Demas, USGS Baton Rouge, pers. commun.). For basic information regarding sampling methodology the reader is referred to Skougstad et al. (1979). The nitrate concentration threshold level was approximately 0.7 mmol/m^3 over the latter portion of the record, and is presumed to be approximately this level for the earlier portion. We have paired monthly water discharge values with the nitrate concentration sampled in that month. The monthly nitrate flux is the product of the once per month nitrate concentrations and the monthly water discharge.

Time series filtering was performed in the frequency domain. Time series were transformed into the frequency domain using a Fast Fourier Transform algorithm, the coefficients of undesired frequencies were set to zero and the series were then inverse transformed resulting in a filtered series in the time domain. Autospectra were formed following Bendat and Piersol (1986). The autospectrum of a time series describes the associated variance as a function of frequency, which allows identification of variance contributions with characteristic time scales.

Three frequency bands were chosen based on analyses of the autospectra: a sub-annual band, with frequencies < 0.075 cycles per month (cpm)
(periods greater than 13.33 months), an annual band, with frequencies between 0.075 and 0.1875 cpm (periods between 13.33 and 5.33 months), and a supra-annual band, with frequencies between 0.1875 and 0.5 cpm (periods between 5.33 and 2.0 months). The annual band includes the annual and semi-annual spectral peaks. The sub-annual band was further divided into narrower frequency bands to help delineate spectral peaks. The lowest frequency band, the very-low-frequency band (VLF), has frequencies < 0.004 cpm (periods greater than 250 months), and will be defined here as the long-term cycle. Detrended data has been filtered to remove this long-term cycle. Significance and confidence levels were determined after Bendat and Piersol (1986).

A predictor/hindcastor analysis was performed using linear optimal estimation theory following the approach used by Davis (1976) to examine the interrelationship and predictability of sea surface temperature and pressure anomalies over the North Pacific Ocean. Linear estimators of some field $P$ were constructed of the form

$$\hat{P} = \sum_{n=1}^{m} \alpha_n d_n$$

where the prediction or hindcast of field $P$ is $\hat{P}$, which is a linear combination of input data variables ($d_n$) multiplied by optimal weights ($\alpha_n$). The fraction of $P^2$ that is accounted for by $\hat{P}$ is called the estimation skill ($S$),

$$S = 1 - \frac{\langle (P - \hat{P})^2 \rangle}{\langle P^2 \rangle}.$$  

Here the $\langle \rangle$'s denote the true temporal or ensemble average value of the enclosed quantity. The skill is optimized in terms of least square error for weights selected such that $\partial S/\partial \alpha_n = 0$ and $S = S_{\text{max}}$.

Davis (1976) provided analytical expressions for the optimal weights assuming several properties of the $P$ field that do not hold true in our case. Most notably the variable fields considered here are non-Gaussian. Linear optimal estimators are often used as a self-consistent method of determining the degree to which a specific "signal" can be predicted or hindcast. For this particular application, we examine the effectiveness of hindcasters for river water discharge, a dominant buoyancy flux component, nutrient concentration, and nutrient flux variations about their long-term temporal average values.

Motivated by the desire to predict the above fields with a known degree of skill and the fact that the historical data seemed to be dominated by persistent, identifiable temporal cycles, we constrained the hindcastor using time varying sinusoids as input data. This form for the input data has the advantages of analytical simplicity, orthogonality and direct results derived from spectra analysis which assumes that the signal under consideration is a composite of sinusoidal functions. The results of this analysis are reported and discussed below.

Results

Time series of monthly Mississippi River water discharge, nitrate concentration and estimated nitrate flux are presented in Fig. 2. Monthly water discharge ranged from 3000 to 42,000 m$^3$/s with a mean of 14,100 m$^3$/s. The most prominent periodic component was the annual cycle, which had an average amplitude of $\sim 15,000$ m$^3$/s. Water discharge also had a smaller-amplitude ($\sim 4500$ m$^3$/s) $\sim 12$ year cycle. Monthly nitrate concentration ranges from the sampling threshold ($< 1$ mmol/m$^3$) to 198 mmol/m$^3$ with a mean of 62.8 mmol/m$^3$. The nitrate concentration had a pronounced long-term cycle ($\sim 36$ year period) with an amplitude of $\sim 60$ mmol/m$^3$. This cycle has a minimum near 1965 and a maximum near 1983; a definite decrease occurred over the earliest decade and the last 6 years of the record. The nitrate concentration also had a definite annual cycle with a $\sim 35$ mmol/m$^3$ amplitude; there was a visible increase in the range of the annual cycle for nitrate concentration over the entire record. The monthly nitrate flux ranges from 9 to 6000 mol/s and had a record mean of 962 mol/s. The annual cycle common to both the nitrate concentration and the water discharge series was also observed in the nitrate flux series. The long-term cycle in nitrate concentration was also apparent.
in nitrate flux as a smaller amplitude cycle, \( \sim 500 \) mol/s. Annual cycle amplitudes were small, \( \sim 500 \) mol/s, during the long-term nitrate concentration minimum and were large, \( \sim 2000 \) mol/s, during the long-term maximum. The overall average amplitude for the annual cycle was \( \sim 1200 \) mol/s.

Linear regression of detrended nitrate concentration against detrended water discharge indicates a statistically significant, positive relationship at the 95% level (Fig. 3). The relationship has a large degree of scatter and the variance explained by the linear model is very low \( (R^2 = 0.07) \). A linear regression using only the filtered annual-band data also shows a weak relationship \( (R^2 = 0.19) \). Log transformation of the river discharge, commonly used in water quality analyses (Davis and Zobrist, 1978), have \( R^2 \) values of 0.12 and 0.13 for the detrended and annual-band data, respectively.

Monthly water discharge, nitrate concentration and nitrate flux were not normally distributed about their annual means (Fig. 4). Probability density function (PDF) estimates of water discharge indicate the mode was nearly one standard deviation below the annual mean value. Minor modes appear at the mean and at one standard deviation above the mean. PDF estimates for nitrate concentration indicate the mode lies between the mean and one standard deviation below the mean, a minor mode lies within one standard deviation above the mean value. PDF estimates of nitrate flux indicate a dominant mode almost one standard deviation below the mean. All three PDF's are biased toward low

![Fig. 2](image1)

![Fig. 3](image2)
values, lowest values were within two standard deviations below the annual mean, while highest values exceeded three standard deviations above the annual mean. Skewness and kurtosis values indicate all three variables had non-Gaussian distributions (Table 1); more variance was contained in the tail with values greater than the mean.

The water discharge auto-spectrum is dominated by a statistically significant peak at the annual frequency (at the 90% level); a lesser peak (not statistically significant) occurs near the subannual frequency corresponding approximately to a four year period (Fig. 5). The nitrate concentration auto-spectrum has a broad statistically significant peak (at the 90% level) about the annual frequency; the long-term cycle is apparent as an increase in variance at the lowest resolvable frequencies (Fig. 5). The nitrate flux auto-spectrum is also dominated by the long-term and annual cycles (Fig. 5). The annual peak is statistically significant at the 90% level. Cross-spectral analysis between water discharge and nitrate concentration indicates statistically significant (at the 95% level) coherence-squared values near two frequency bands, the annual band and the supraannual band corresponding to a period of about four months (Fig. 6). The water discharge leads

![Graphs](image)

Fig. 4. Probability density functions of Mississippi River water discharge (upper), Mississippi River nitrate concentration (center) and associated nitrate flux (lower). Arrow and vertical bars represent sample annual means and ± one standard deviation, respectively.

![Graphs](image)

Fig. 5. Auto-spectra of Mississippi River monthly averaged water discharge (left), Mississippi River nitrate concentration (center), and associated nitrate flux (right). Confidence limits indicate the 95% significance level. Degrees of freedom are 10.

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**Table 1**

- **Water Discharge**: Mean ± Standard Deviation
  - Mean: 1.5 x 10^3 m³/s
  - Standard Deviation: 0.5 x 10^3 m³/s

- **Nitrate Concentration**: Mean ± Standard Deviation
  - Mean: 20 mmol/s
  - Standard Deviation: 10 mmol/s

- **Nitrate Flux**: Mean ± Standard Deviation
  - Mean: 5000 mol/s
  - Standard Deviation: 5000 mol/s
TABLE 1
Mean, standard deviation ($S_d$), coefficient of variation (CV), skewness, kurtosis and hindcastor skills for time series of water discharge (Tarbert Landing, MS), nitrate concentration (St. Francisville, LA) and associated nitrate flux. Hindcastor skills are presented for predictions using the annual (A), very-low-frequency (VLF), and both the annual and the very-low-frequency (A + VLF) cycles. Normal distributions have skewness and kurtosis values of 0.0 and 3.0, respectively. Estimated skills below the threshold (~0.1) associated with random correspondence or artificial hindcastor skill are indicated by ****. Perfect estimators have skill = 1.0; skill cannot be less than zero.

<table>
<thead>
<tr>
<th></th>
<th>Water discharge (m$^3$/s)</th>
<th>Nitrate concentration (mmol/m$^3$)</th>
<th>Nitrate flux (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>14100</td>
<td>62.8</td>
<td>962</td>
</tr>
<tr>
<td>$S_d$</td>
<td>7800</td>
<td>38.1</td>
<td>891</td>
</tr>
<tr>
<td>CV</td>
<td>0.55</td>
<td>0.60</td>
<td>0.93</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.93</td>
<td>0.90</td>
<td>1.84</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>3.29</td>
<td>3.51</td>
<td>7.60</td>
</tr>
<tr>
<td>Hindcastor skill</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.44</td>
<td>****</td>
<td>0.27</td>
</tr>
<tr>
<td>VLF</td>
<td>****</td>
<td>0.50</td>
<td>0.26</td>
</tr>
<tr>
<td>A + VLF</td>
<td>0.46</td>
<td>0.48</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Results of the linear optimal estimator analysis are presented in Table 1. The specific form of the estimators used is

$$\hat{\mathbf{P}} = \alpha_1 \cos(x_1 t + \phi_1) + \alpha_2 \cos(x_2 t + \phi_2).$$

The indices (1 and 2) refer to the annual and the long-term cycles, respectively, with associated amplitudes ($\alpha_i$), frequencies ($x_i$) and phases ($\phi_i$). The cycle period selection was motivated by the results of the spectral analysis and by qualitative examination of the time series themselves.

The estimator skill values indicate the hindcastor skills are greatest for water discharge and nitrate concentration if a single component estimator is employed (Table 1); i.e., the annual cycle for the water discharge and the long-term cycle for the nitrate concentration. The nitrate flux estimator skill is equally partitioned between annual and the long-term components. The best
TABLE 2
Total and frequency band variances of monthly mean Mississippi River water discharge (Tarbert Landing, MS), monthly sampled Mississippi River nitrate concentration (St. Francisville, LA), and nitrate flux. Data cover August 1954 through December 1990. Frequency bands are described in cycles-per-month (cpm)

<table>
<thead>
<tr>
<th></th>
<th>Water discharge variance</th>
<th>% Total</th>
<th>Nitrare variance</th>
<th>% Total</th>
<th>Nitrare flux variance</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($10^7$ m$^6$ s$^{-2}$)</td>
<td></td>
<td>($10^{-5}$ mol$^2$ m$^{-6}$)</td>
<td></td>
<td>($10^5$ mol$^2$ s$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>6.08</td>
<td>146.2</td>
<td>7.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total sub-annual band (&gt; 0.075 cpm)</td>
<td>1.52</td>
<td>25.0</td>
<td>98.19</td>
<td>67.2</td>
<td>3.52</td>
<td>44.3</td>
</tr>
<tr>
<td>Separate sub-annual bands</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(&gt; 0.004 cpm)</td>
<td>0.14</td>
<td>2.3</td>
<td>77.90</td>
<td>53.3</td>
<td>2.21</td>
<td>27.8</td>
</tr>
<tr>
<td>(0.004-0.01 cpm)</td>
<td>0.30</td>
<td>4.9</td>
<td>4.31</td>
<td>2.9</td>
<td>0.28</td>
<td>3.5</td>
</tr>
<tr>
<td>(0.01-0.03 cpm)</td>
<td>0.65</td>
<td>10.7</td>
<td>5.48</td>
<td>3.7</td>
<td>0.46</td>
<td>5.8</td>
</tr>
<tr>
<td>(0.03-0.045 cpm)</td>
<td>0.14</td>
<td>2.3</td>
<td>3.63</td>
<td>2.5</td>
<td>0.12</td>
<td>1.5</td>
</tr>
<tr>
<td>(0.045-0.075 cpm)</td>
<td>0.30</td>
<td>4.9</td>
<td>6.88</td>
<td>4.7</td>
<td>0.45</td>
<td>5.7</td>
</tr>
<tr>
<td>Annual band (0.075-0.1875 cpm)</td>
<td>3.66</td>
<td>60.2</td>
<td>29.02</td>
<td>19.8</td>
<td>3.57</td>
<td>45.0</td>
</tr>
<tr>
<td>Supra-annual band (&lt; 0.1875 cpm)</td>
<td>0.86</td>
<td>14.1</td>
<td>19.01</td>
<td>13.0</td>
<td>0.85</td>
<td>10.7</td>
</tr>
</tbody>
</table>

estimator for all the quantities account for 40–50% of the variance in the signal. These are substantial skill levels considering that the 95% confidence limit for non-zero skill is conservatively estimated to be 0.1. This level ($S = 0.1$) can also serve as an estimate of the “artificial” skill associated with the fact that there is likely to be random, coincidental correlation between signals with comparable frequency content.

True forecast skill can be approximated (even before a single forecast is made) by subtracting the estimated “artificial” skill from the observed hindcast skill [c.f. Davis (1976) for a discussion and details]. Therefore, these results indicate the underlying forecast skills for variance in these fields probably range from 0.3 to 0.4.

Discussion

We have shown that the probability density functions associated with water discharge, nitrate concentration and nitrate flux in the lower Mississippi River are significantly skewed and non-Gaussian. The statistical modes are less than the means which implies that randomly selected samples will tend to be biased below their means and that sample values greater than two standard deviations above the means are significantly more likely than expected for Gaussian fields. These density functions are better described by Poisson random functions.

There is a weak linear relationship between water discharge and nitrate concentration. There was similarity between the annual cycles of water discharge and nitrate concentration; highest nitrate concentrations usually occurred during the vernal freshet, and lowest concentrations usually occurred along with autumnal low flow conditions. Very little river discharge variation was attributed to the lowest frequencies resolved where most of the nitrate concentration variation occurred, hence the low correlation coefficient. Cross-spectral analysis indicates nitrate concentration was significantly coherent with water discharge only at the annual cycle, with nitrate lagging water discharge by one month. This lag is an average statistic and the result of the temporal and spatial relationships between river flooding and the relative nitrate loading in the major tributaries.
One explanation for this lag is that the initial flood stage is associated with an early snow melt, which is nutrient poor, compared to the later thaw water, and precedes the period of runoff carrying agricultural fertilizers. Another would be that the first tributary basin to “thaw”, and show up downstream on the lower Mississippi River as a high discharge, was usually nitrate poor compared to subsequent basin discharge of relatively nitrate rich water. The actual temporal and nutrient loading relationships would have to be determined, using data sets comparable to the ones used here if available, for upriver locations and for locations on each of the major distributaries.

The inter-annual variations between nitrate concentration and water discharge were incoherent. This produced large scatter in the data and was manifest in the linear regression relationships as low correlations. Even at the annual cycle, where there was significant coherence between water discharge and nitrate concentrations (Fig. 6), there remains a large amount of apparently unrelated variation.

Some of this variation may be due to sampling bias in the data as instantaneous nitrate concentration values were taken by necessity to be characteristic of an entire month. Aliasing by variations at unresolved periods, i.e., periods less than two months, occurred for the resolved periods of variation; we have no way of describing these variations in any detail in our study period using historical data.

Only recently has water quality data been acquired for the lower Mississippi River that can address the variations of approximately weekly nitrate concentration sampling (Goolsby et al., 1991). Three months of twice-per-week data, from a USGS study of Mississippi River water quality, indicated that nitrate concentrations at St. Francisville, LA had standard deviations of 6-11% about the monthly mean. Monthly water discharge values for the 35 year record, thought to be relatively accurate estimators of a given month’s discharge, had standard deviations of daily Mississippi River discharge which ranged from 5% of the monthly mean, during times of relatively constant flow, to 20%, during times of large flow fluctuations. Based on this information we infer that the longer period nitrate concentration variations have amplitudes that were well above the shorter period “noise” of the monthly nitrate data, and that the shorter period “noise” of the monthly nitrate data is about the same relative amplitude as that for the water discharge.

Comparison of USGS nitrate concentration values data used in this analysis and data sampled by the Louisiana Department of Environmental Quality (LA-DEQ) (1980–1989) show similar magnitude values for samples collected within one week of each other. Sample regime-induced differences were inseparable from natural variations due to dissimilar sampling schemes. USGS data were true cross-sectional averages; the LA-DEQ values were single surface values from both river banks.

Time-of-travel studies indicated that complete lateral dispersion was achieved after excursions of only 40 km on the lower Mississippi River (Weber, 1980). This is equivalent to an advective interval of approximately one day. Based on the time-of-travel study, the small variations of the recent, frequently sampled USGS nitrate concentration data, and on the ambiguous results of data comparison between different agencies, we assumed that the Mississippi River at St. Francisville, LA, is reasonably well mixed for the nitrate concentration variations over weekly time periods. Sampling-induced differences were relatively small compared to seasonal changes regardless of whether differences were due to small-scale spatial variations or to other sources. If the “noise” variations were unbiased about the mean, our results are somewhat insensitive to this level of random sampling error. In any case, it is impossible to “undo” a historical sampling regime. A well-focused sampling design experiment would help sort out some of these points and should be considered.

The long-term trend in nitrate concentration appears as a 36-year sinusoid and indicates a two-fold increase from the 1960’s to the 1980’s. This single 36-year cycle may be a unique occurrence in the record. It should not be interpreted as a continuously repeating cycle. The general increase, though, has also been noted by Walsh et al. (1981) and Turner and Rabalais (1991). Turner
and Rabalais (1991) attribute a portion of this increase to the increased use of agricultural fertilizers in the United States. Smith et al. (1987) suggest that atmospheric deposition may play a primary role in this long-term variability. In a river system as large and as complex as the Mississippi River system, the nitrate concentration measured in the lower river is the sum of various upstream contributors. The complex hydrologic relationships between the major tributaries as well as the relative spatial and temporal contributions from agricultural, industrial and urban sources, makes the total nutrient loading in the lower Mississippi River difficult to identify by source.

Increased use of agricultural fertilizer has been hypothesized as the explanation for increased nitrate concentrations over the last 40 years. If this hypothesis is true, what then, is the explanation for the nitrate flux minimum in the early 1960's? A minimum can only occur after a period of decreasing values. One can speculate that industrial and urban contributions to the nitrate concentration have also increased in the post World War II years, but a consistent, monotonically increasing nitrate flux trend conflicts with the observed time history of nitrate flux in the lower Mississippi River.

The nitrate flux time series must have the major attributes of both the water discharge and the nitrate concentrations; a long-term cycle and an annual cycle. Total nitrate flux is one important component in driving primary production in the coastal Gulf of Mexico. Annually integrated nitrate flux is equivalent to the mass of nitrogen (as nitrate) delivered by the Mississippi River to the Gulf of Mexico over one year. Walling and Webb (1985) found that computing annual flux values as the product of long-term average values underestimated the total flux in a small river system in England. Even weighting the average concentrations with monthly average water discharge underestimated the total flux determined as the product of daily concentration and water discharge. Since variability for nitrate concentration and water discharge is coupled in the lower Mississippi River, the annual average of the product is 7% greater than the product of average values, averaged over the 35 year record. The true annual nitrate flux, one determined from daily nitrate concentration and water discharge values, would be somewhat higher than the flux determined using the values here. Also note that there are potential sources of nutrients that would add to the total nitrate load downstream of the nitrate concentration sampling site at St. Francisville, LA, the New Orleans metropolitan area, and the industrial corridor along the Mississippi River.

The linear optimal estimator analysis indicates that a substantial percentage of the signal variances could be hindcast (40–50%) or potentially predicted (30–40%). The estimators employed rely upon no more than historical data. Practical forecasters for these fields would be based upon the long-term historical mean values for a given field plus a time variable component similar to those used in this analysis. Since the coefficients of variation for these fields range between 0.5 and 1.0, and the estimated prediction skill for variations from the mean is $\sim 0.3$, the total signal (mean and variations) can be predicted with a high degree of skill (0.5–0.8). The difference between estimated hindcast skills and prediction skills is the "artificial" skill associated with coincidental agreement between time sequences of limited duration and comparable frequency content.

**Summary**

We have analyzed 35 years of monthly sampled, time-sequence data of Lower Mississippi River water discharge, nitrate concentration and nitrate flux. We have also explored the degree to which predictions of water discharge, nitrate concentration and nitrate flux can be made. The estimated probability density function for these variable fields were non-Gaussian and better represented by Poisson distributions. These results indicate a large amplitude, dominant long-term cycle in the nitrate concentration that is not observed in the water discharge. A decrease in average nitrate concentration from the 1983 peak to the present reinforces the idea that this variability is better described by sinusoidal rather
than linear or quadratic functions. River-water discharge variation was greatest in association with the annual cycle. The annual cycles were similar in water discharge and nitrate concentration; higher nitrate concentrations usually occurred during the vernal freshet, and low concentrations usually occurred along with autumnal low-flow conditions.

Despite this qualitative similarity, linear regression analyses revealed that the quantitative covariability between these two fields was weak ($R^2 < 0.19$), even if detrended data sequences were used. Variability in nitrate flux time history reflected the combined influences of a dominant long-term cycle and a secondary annual cycle in nitrate concentration and a dominant annual cycle in water discharge.

A linear optimal estimator analysis showed that there was significant hindcast (and forecast) skill for water discharge, nitrate concentration and nitrate flux. Since the estimator constructs consisted of one or two simple sinusoids of different frequencies, and therefore have relatively few free parameters, there is reason to believe that truly skilled forecasts (with 30–40% of the variance accounted for) of all three fields are technically feasible.

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