Lower Mississippi River historical nitrate flux and Mississippi River outflow buoyancy flux

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Abstract

Results from an analysis of 35-year time sequences of Lower Mississippi River water discharge, nitrate concentration and nitrate flux are discussed. The potential predictability of these quantities is evaluated. Results indicate a large amplitude, very-low-frequency 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 is greatest in association with the annual cycle. The annual water discharge and nitrate concentration cycles are similar, high nitrate concentrations usually occur near the spring freshet and low concentrations usually occur along with autumn low flow conditions. Nitrate flux variations exhibit a low amplitude, very-low-frequency modultation of a dominant, annual cycle. A predictor-hindcastor analysis indicates that truly skilled forecasts of all three fields are feasible.

Shelf stratification and nutrient field conditions respond to forcing by riverine source functions. Hydrographic data in the Mississippi River outflow region from two NECOP cruises are presented. Spatial distributions of Cruise 1 (summer 1990) and Cruise 2 (winter 1991) hydrographic data are compared seasonally and with historical data. Shelf stratification conditions are examined based on NECOP cruise data, and these conditions are discussed in the context of riverine and other forcing functions.

The Mississippi River system drains approximately 41 percent of the contiguous United States, with an average water discharge that ranks first in North America and seventh in the world (van der Leeden et al., 1990). 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). Monthly nitrate concentration values also progress through a less distinct annual cycle with high values in the spring and lows in the fall. This annual cycle is similar to the characteristic annual Mississippi River water discharge cycle. The ecological implications to the coastal waters of the northern Gulf of Mexico are many, some of which are changing primary production (Lohrenz *et al.*, 1990), possible association with near-bottom, low dissolved oxygen regions in the adjacent shelf regions (Turner *et al.*, 1987), and species succession due to changes in nutrient levels (Turner and Rabalais, 1991). 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 predictability of nitrate flux, nitrate concentration and water discharge using linear optimal estimator analysis (Dinnel and Bratkovich, 1990 and manuscript submitted).

Mississippi River nitrate data was extracted from U.S. Geological Survey (USGS), Surface Water Quality Reports for the station at or near St. Francisville, La., (U.S. Department of the Interior, 1964-1990), data from 1954-1963 was reported by Walsh *et al.*, (1981). Samples were begun in 1954 and continued through September 1990. St. Francisville is approximately 450 km upstream from the Mississippi River Delta. Mississippi River water discharge data at Tarbert Landing, 480 km upstream from the Mississippi River Delta, was reported by the U.S. Army, Corps of Engineers (USACOE). There are no major tributaries downstream of this gauging station on the Mississippi River.

The nitrate concentrations used were essentially instantaneous values, sampled at approximately monthly intervals; water discharge data were monthly averages of daily values. We have paired the nitrate concentrations with the water discharge for each month. Although we expect nitrate concentrations to fluctuate over short periods, we cannot describe these variations and, therefore, assumed that the instantaneous concentrations were reasonably characteristic for the entire month. The monthly average water discharge data are relatively accurate estimators of a given month's discharge. Standard deviations of daily values range from 5 to 20 percent of the monthly means. The monthly nitrate flux is the arithmetic product of instantaneous nitrate concentrations and the monthly average water discharge.

Analysis and filtering of time series were performed using a Fast Fourier Transform (FFT) algorithm. Filtering was performed in the frequency domain. 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

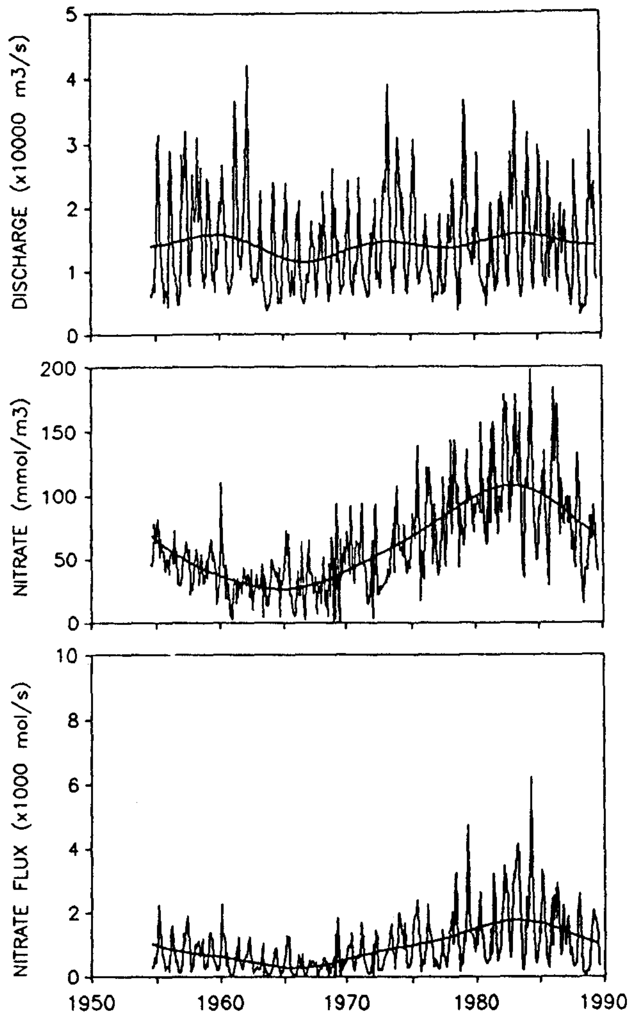

Figure 1. Monthly and very-low-passed times series of Mississippi River water discharge, Tarbert Landing, Miss. (upper), Mississippi River nitrate concentration near St. Francisville, La. (center), and associated nitrate flux (lower) (Dinnel and Bratkovich, submitted).

between 0.1875 and 0.5 cpm (periods between 5.33 and 2.0 months). The sub-annual band was further divided into narrower frequency bands to help delineate spectral peaks. The very-low-frequency band (VLF), with frequencies <0.004 cpm (periods greater than 250 months), is defined as the long-term trend.

A predictor/hindcastor analysis was performed using linear optimal estimation theory following Davis (1976). This approach is 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 hindcastors for river water discharge, nutrient concentration and nutrient flux variations about their long-term temporal average values. Motivated by the need to predict the above fields with a known degree of skill and the fact that the historical data seemed to be dominated by 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 relevance to spectrally derived results.

Time series of monthly Mississippi River water discharge, nitrate concentration and associated nitrate flux are presented in Fig. 1. Monthly water discharge has a prominent annual cycle and smaller-amplitude VLF cycle (~12 year period). The nitrate concentration has a pronounced VLF cycle (~36 year period). This VLF cycle has a minimum near 1965 and a maximum near 1983; a definite decrease occurred over the earliest decade and the last six years of the record. The nitrate concentration also has an definite annual cycle. The annual cycle common to both nitrate concentration and water discharge is also observed in the nitrate flux (Fig. 2).

Linear regression of detrended nitrate concentration against detrended water discharge indicates a statistically significant, positive relationship at the 95 percent level; scatter is large, R^2=0.07. A linear regression using the annual-band data also shows a significant but marginal relationship (R^2=0.19).

Monthly water discharge, nitrate concentration and nitrate flux are not normally distributed about their annual means (Fig. 3). All three probability density functions (PDFs) are biased toward low values, lowest values are within two standard deviations below the annual mean, while highest values exceed three standard deviations above the annual mean. Skewness values are 0.98, 0.90, and 1.85 for water discharge, nitrate concentration and nitrate flux, respectively.

The water discharge, nitrate concentration and nitrate flux auto-spectra are dominated by statistically significant peaks at the annual frequency (at the 90 percent level). Cross-spectral analysis between water discharge and nitrate concentration indicates statistically significant (at the 95 percent level), coherence-squared values near the annual band, where the water discharge leads the nitrate concentration by approximately one month.

More than 60 percent of the water discharge total variance is contained within the annual band, with only 25 percent contained in the sub-annual bands and a lesser amount in the supra-annual band (Table 1). More than 67 percent of the nitrate concentration total variance is contained in the sub-annual band, with 54 percent of the total variance contained in the VLF band associated with the long-term cycle. The nitrate flux band-limited variances reflect both the water discharge and the nitrate concentration variance patterns.

Results of the linear optimal estimator analysis are presented in Table 2. The specific form of the estimator used is $P = \alpha_1\cos(\omega_1 t+\phi_1)+\alpha_2\cos(\omega_2 t+\phi_2)$. The indices (1 and 2) refer to the annual and the very low-frequency cycles, respectively, with associated amplitudes, α_i, frequencies, ω_i, and phases, ϕ_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, shown in Table 2, indicate the hindcastor skills are greatest for water dis-

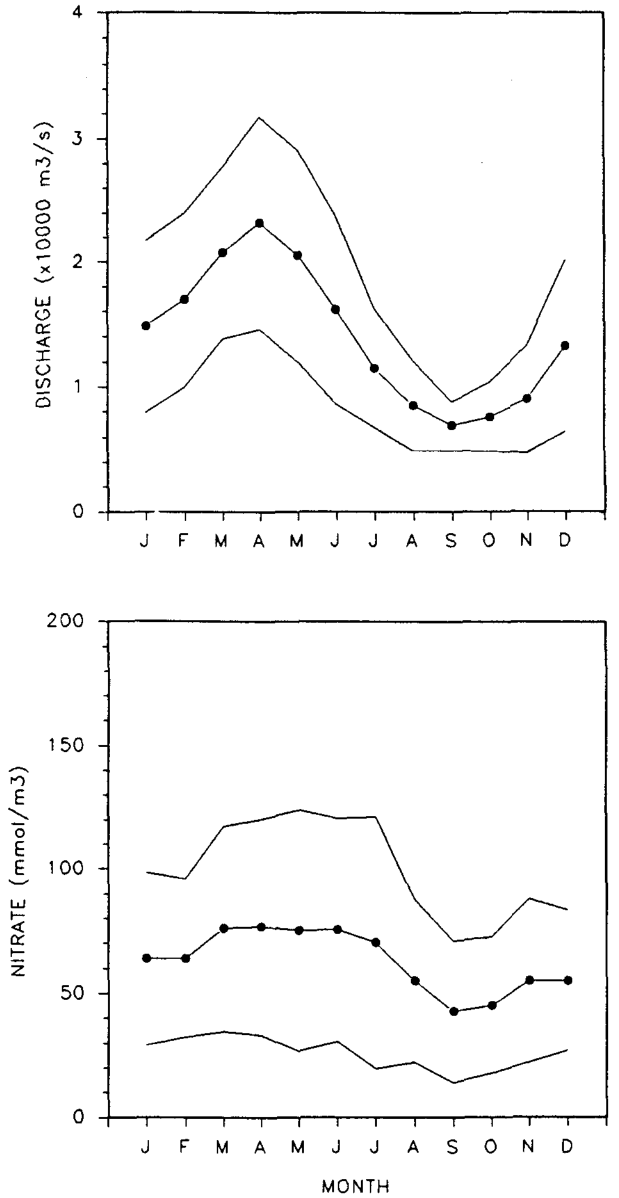

Figure 2. Annual cycle of average monthly Mississippi River water discharge, Tarbert landing, Miss. (upper) and Mississippi River nitrate concentration near St. Francisville, La. (lower), plus and minus one standard deviations are shown.

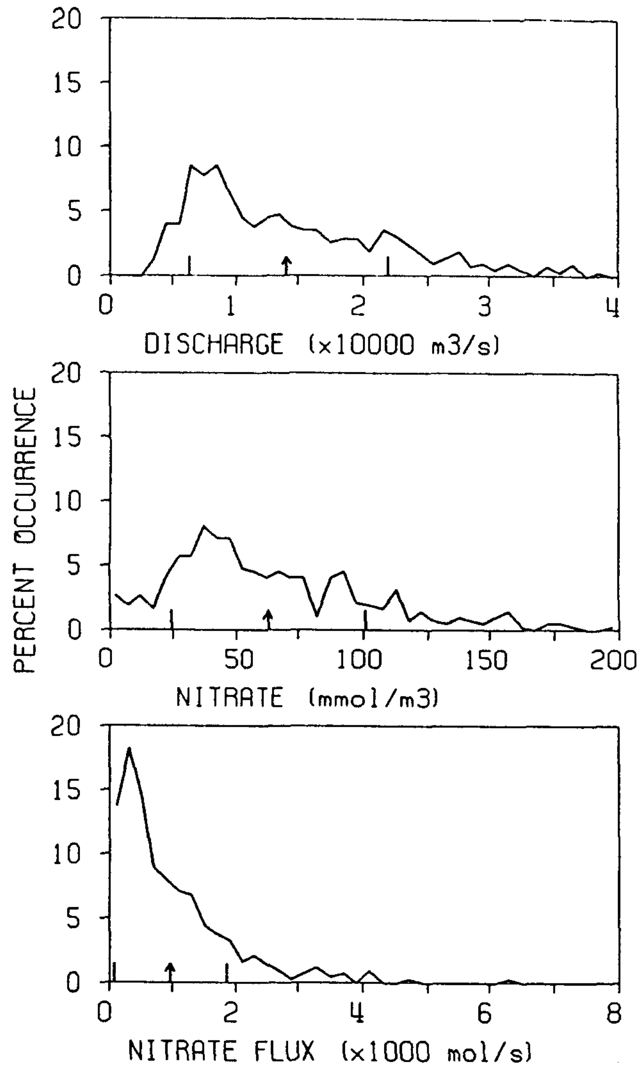

Figure 3. Probability density functions of Mississippi River water discharge (upper), Mississippi River nitrate concentration (center), and associated nitrate flux (lower). Arrow and vertical bars represent sample annual means and one standard deviation, respectively (Dinnel and Bratkovich, submitted).

charge and nitrate concentration if a single component estimator is employed; 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 estimator for all the quantities account for 40 to 50 percent of the variance in the signal. These are substantial skill levels considering the point that the 95 percent confidence limit for non-zero skill is conservatively estimated to be 0.1 on one- to five-year time scales.

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. These results indicate a large amplitude, dominant very-low-frequency (VLF) 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 confirms that this variability is more cyclic than trend-like. River water discharge variation is greatest in association with the annual cycle. The annual cycles are similar in water discharge and nitrate concentration, high nitrate concentrations usually occur during the spring freshet and low concentrations usually occur along with autumnal low-flow conditions.

Despite this qualitative similarity, a linear regression analysis revealed that the quantitative covariability

Table 1. Variance of monthly mean Mississippi River water discharge (Tarbert Landing, Miss.) and monthly sampled Mississippi River nitrate concentration (St. Francisville, La.) from August 1954 through December 1990 (Dinnel and Bratkovich, submitted).

	Water Discharge Variance ($10^7 m^6 s^{-2}$)	Percent Total	Nitrate Variance ($10^{-7} mol^2 m^{-6}$)	Percent Total	Nitrate Flux Variance ($10^5 mol^2 s^{-2}$)	Percent Total
Total	6.084		146.228		7.937	
Total Sub-annual Band						
(>0.075 cpm)	1.521	25.0	98.190	67.1	3.517	44.3
Separate Sub-annual Bands						
(>0.004 cpm)	0.144	2.4	77.895	53.3	2.213	27.9
(0.004-0.01 cpm)	0.297	4.9	4.310	2.9	0.280	3.5
(0.01-0.03 cpm)	0.648	10.7	5.478	3.7	0.455	5.7
(0.03-0.045 cpm)	0.136	2.2	3.628	2.5	0.118	1.5
(0.045-0.075 cpm)	0.296	4.9	6.879	4.7	0.451	5.7
Annual Band						
(0.075-0.1875 cpm)	3.663	60.6	29.020	19.8	3.568	45.0
Supra-annual Band						
(<0.1875 cpm)	0.864	14.3	19.014	13.0	0.852	10.7

Table 2. Means, standard deviations (S_d), coefficients of variation (CV), and hindcastor skills for time series of water discharge (Tarbert Landing, Miss.), nitrate concentration (St. Francisville, La.) and associated nitrate flux. Hindcastor skill are presented for predictions using the annual (A), very-low-frequency (VLF), and both the annual and the very-low-frequency cycles. Estimated skills below the threshold (~0.1) associated with random correspondence or artificial hindcastor skill are indicated by ** (Dinnel and Bratkovich, submitted).**

	Mean	S_d	CV	Hindcastor Skill A	Hindcastor Skill VLF	Hindcastor Skill A+VLF
Water Discharge (m^3/s)	14100	7800	0.55	0.44	****	0.46
Nitrate Concentration ($mmol/m^3$)	62.8	38.1	0.60	****	0.50	0.48
Nitrate Flux (mol/s)	961.84	890.55	0.93	0.27	0.26	0.49

Note: Perfect estimators have skill = 1.0; skill cannot be less than zero.

between these two fields was weak (R2<0.15), even if filtered versions of the data sequences were used. Variability in nitrate flux time history reflected the combined influences of the dominant VLF cycle in nitrate concentration and the dominant annual cycle in water discharge. Low amplitude modulation in the annual cycle was evident.

A linear optimal estimator analysis showed that there was significant hindcastor (and forecastor) skill for water discharge, nitrate concentration, and nitrate flux. Since the estimator constructs consist of one or two simple sinusoids with offset frequencies, there is reason to believe that truly skilled forecasts of all three fields are feasible over times scales of several months to several years.

Daily Mississippi River discharge for 1990 and 1991 is presented to define the discharge environment of the two field sampling cruises. Cruise I followed the spring freshet discharge decline by approximately one month. The outflow region was associated with discharge values near the long-term mode, approximately 10,000 $m^3 s^{-1}$, less than one standard deviation below the annual mean. Cruise II occurred during the 1991 spring freshet. The outflow region was associated with the smaller of three peaks in the spring flood, discharge values were approximately 25,000 $m^3 s^{-1}$, slightly greater than one standard deviation above the annual mean (see Fig. 3).

Using historical hydrographic data from the RV *GUS*, Bureau of Commercial Fisheries, shelfwide surveys in the early 1960s, we have been able to estimate the fill time of the Louisiana Bight region (Fig. 4). This region is defined as the shelf (depth <100 m) west of the delta to approximately 90.5°W. Fill time represents a time-dependent estimate of residence time. It is determined by summing the fresh water inputs backward in

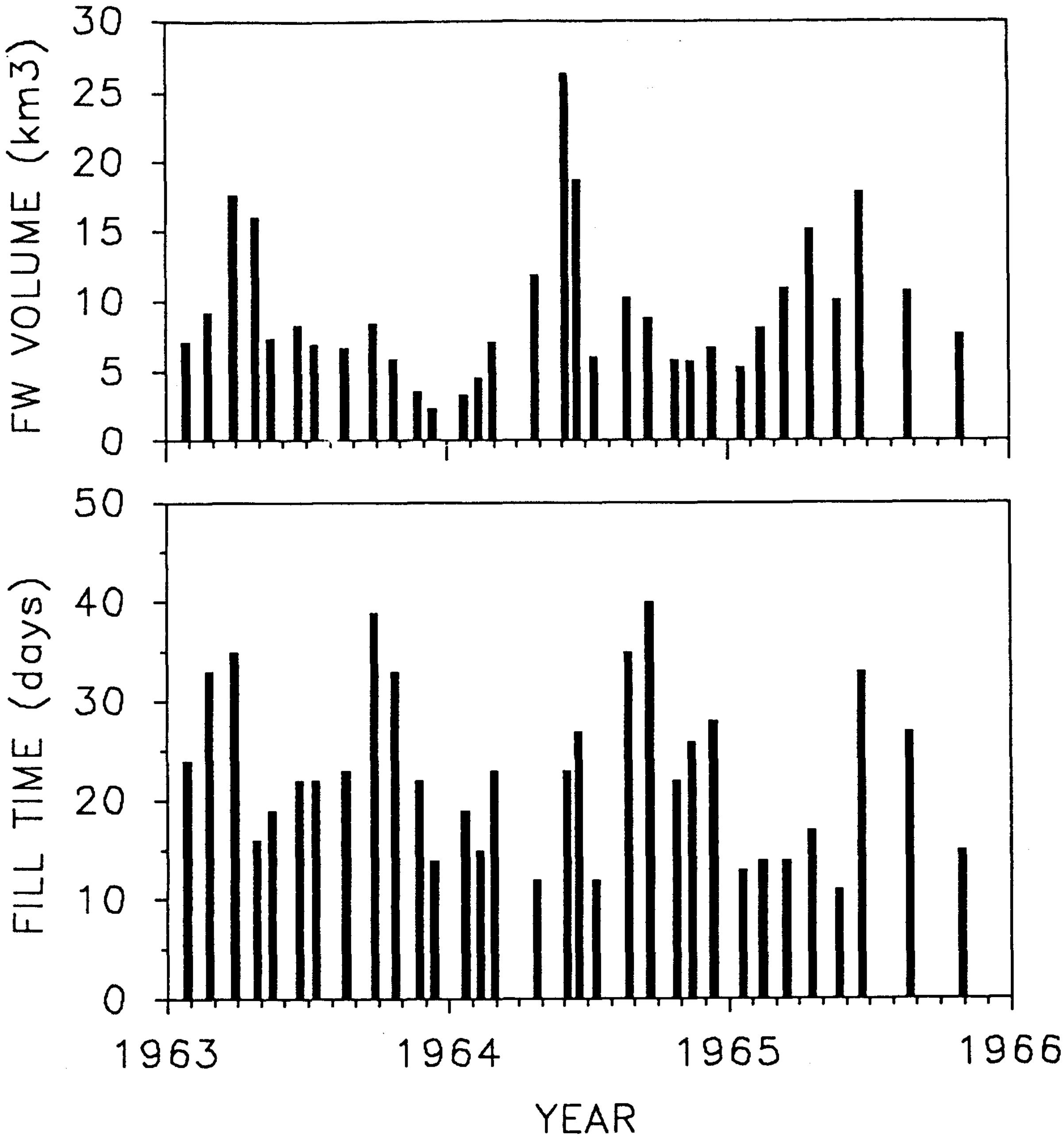

Figure 4. Louisiana Bight fresh water volume and fill times 1963-1965, based on upper 37.5 m of water column.

time to account for an estimated shelf freshwater volume (Dinnel and Wiseman, 1986). Freshwater volume in the upper 37.5 m of the Louisiana Bight is closely tied to discharge levels. Fill times were short, between 15 and 40 days, with an average less than one month. This implies that the outflow region has, at times a very short residence time (0.5 month) of Mississippi River discharge when the river is in flood; and an approximate one-month memory of past discharge at times of lower flow.

Salinity fields for NECOP Cruise I and II were presented. During Cruise I (lower river discharge), the surface (1 m) salinities were lowest (~17‰) near mouth of Southwest Pass, graded to open-Gulf of Mexico values (>36‰) 50 km offshore, and to upper 20's in the western portion of the sampled region (100 km west). Salinities at 10 m depth showed similar distributions but were 8 to 10‰ greater. Salinity fields during the first leg of Cruise II show a very similar surface pattern as Cruise I, with almost identical salinity values. Lowest salinity values were nearest the delta and graded to less than open Gulf values offshore and westward (~32‰). Over the shelf, salinities at 10 m graded from low to higher values seaward, and also never reached open Gulf values.

In the immediate future we intend to estimate freshwater volume and fill times for NECOP Cruise I and II data and to relate them to the historical analyses. Based on comparisons to RV GUS data and on time series data we expect freshwater volume and fill times to range from 5 to25 km^3 and 15 to 30 days, respectively.

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