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Mississippi River Nitrate Loads from High Frequency Sensor Measurements and Regression-Based Load Estimation

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Supporting Information

ABSTRACT: Accurately quantifying nitrate (NO_3^-) loading from the Mississippi River is important for predicting summer hypoxia in the Gulf of Mexico and targeting nutrient reduction within the basin. Loads have historically been modeled with regression-based techniques, but recent advances with high frequency NO_3^- sensors allowed us to evaluate model performance relative to measured loads in the lower Mississippi River. Patterns in NO_3^- concentrations and loads were observed at daily to annual time steps, with considerable variability in concentration-discharge relationships over the two year study. Differences were particularly accentuated during the 2012 drought and 2013 flood, which resulted in anomalously high NO_3^- concentrations consistent with a large flush of stored NO_3^- from soil. The comparison between measured loads and modeled loads (LOADEST, Composite Method, WRTDS) showed underestimates of only 3.5% across the entire study period, but much larger differences at shorter time steps. Absolute differences in loads were typically greatest in the spring and early summer critical to Gulf hypoxia formation, with the largest differences (underestimates) for all models during the flood period of 2013. In additional to improving the accuracy and precision of monthly loads, high frequency NO_3^- measurements offer additional benefits not available with regression-based or other load estimation techniques.

INTRODUCTION

The nitrogen (N) load from the Mississippi River—which drains 41% of the continental United States—has increased significantly during the past 100 years and is one of the primary causes of the summer hypoxia in the Gulf of Mexico.[1,2] Nitrate (NO_3^-) has been the dominant form of increased N loading since the 1970s.[3] Accurately quantifying NO_3^- loading to the Gulf and understanding how it interacts with ocean processes to determine the size of the hypoxic zone is a major objective of the Mississippi River Action Plan, with a goal of reducing the 5-year average size to 5000 km^2 or less by 2015.[4]

The loads of NO_3^- to the Gulf have historically been modeled using a regression-based estimation technique (LOADEST) that predicts nutrient concentrations through time from relatively infrequent discrete samples and high frequency discharge measurements.[5] The output from this and other regression-based models have not only been important for predicting the size of the summer hypoxic zone,[6] but it has also been used to evaluate trends in nutrient loading over time[7] and with climate variability.[8] However, recent advances in in situ NO_3^- sensors provides an opportunity to measure changes in concentration at much higher temporal frequencies (e.g., many times per hour or day). High frequency NO_3^- data have proven useful for quantifying diel and event N dynamics,[9−11] as well as for real-time monitoring of drinking water and wastewater discharge. However, high frequency NO_3^- data may also improve the accuracy and precision of load estimates by reducing sample bias and uncertainties inherent in statistically modeled values.[12]

Here we present an analysis of high temporal frequency NO_3^- measurements in the lower Mississippi River at Baton Rouge over two years (November 2011 to October 2013) and compare measured NO_3^- loads to those from three regression-based load estimation models. This deployment captured a transition from an extreme summer drought in 2012 to spring flooding in 2013, a pattern which has been shown in previous studies to result in large N loads to the Gulf of Mexico and subsequently the largest hypoxic zones.[3,13−16] The specific objectives were to (1) assess the timing and magnitude of

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variability in NO_3^- concentrations and loads in the lower Mississippi River, and (2) compare measured monthly NO_3^- loads from the Mississippi River with modeled loads from three regression-based techniques (LOADEST, Composite Method and WRTDS) developed for use with relatively infrequent discrete measurements. We also evaluate the benefits of high frequency NO_3^- data for understanding riverine N loading and Gulf hypoxia. Addressing these objectives will highlight the potential value of high temporal frequency data generated by NO_3^- sensors and may help with developing effective programs to reduce nutrient loads.

MATERIALS AND METHODS

Site Description. The Mississippi River drains 41% of the conterminous United States (3.27×10^6 km^2) and includes all or parts of 30 states. The river mainstem is 3700 km in length and runs from the southern Canadian border to the Gulf of Mexico. The climate, land use, soils and population vary widely across the basin,[3] but the dominant land use is agriculture (58% of the basin area). Agricultural production is particularly intense within the central part of the basin, which produces the majority of the corn, soybeans, wheat, cattle, hogs and chickens grown in the U.S. Other important land uses include range and barren land (21%), woodland (18%), wetlands and water (2.4%) and urban land (0.6%).[3]

An in situ NO_3^- sensor was deployed in November 2011 in the Mississippi River at Baton Rouge (USGS gage 07374000), which is 370 km from the Gulf of Mexico and drains a total area of 2.91×10^6 km^2. Baton Rouge is 130 km below Old River Control, where approximately 30% of the combined flow from the Mississippi and Red Rivers is diverted to form the headwaters of the Atchafalaya River. The deployment site is also 52 km downstream of St. Francisville (USGS gage 07373420), a long-term USGS National Water Quality Assessment (NAWQA) monitoring site on the Mississippi River with a history of 30+ years of discrete water quality data collection. The discharge at the Baton Rouge gage has been measured since 2004 along with continuous water quality measurements of dissolved oxygen, temperature, turbidity, specific conductance and pH (YSI 6920 sonde; Yellow Springs, OH).

High Frequency NO_3^- Sensor Measurements. A submersible ultraviolet nitrate analyzer (SUNA) with a 10 mm optical path length (Version 1; Satlantic, Nova Scotia, Canada) was mounted on an instrument cage along with a custom submersible CR1000 datalogger (Campbell Scientific, Logan, Utah) and ancillary electronics. The instrument cage was deployed vertically on a fixed I-beam from a pier on the eastern bank of the Mississippi River and was maintained at a fixed depth that ensured at least 1 m of water above the sensor at all times. The SUNA collected data every 15 min initially, but was later adjusted to measure every 3 h to conserve power while still capturing the temporal variability in NO_3^- concentrations. The SUNA was operated in freshwater mode (i.e., without bromide temperature compensation) and included an external nylon brush wiper (Zebra-Tech, New Zealand) that cleaned the optical windows prior to every sampling interval. Sensors were checked for blanks and linearity prior to and during deployment as described in Pellerin et al.[17]

In situ NO_3^- concentrations were measured by the SUNA at a sampling rate of ~1 Hz over a 30 s burst window at each sampling interval, which typically resulted in ~20 measurements of NO_3^- concentrations per burst. Outliers within the burst were eliminated based on the median absolute deviation[18] and burst statistics (mean, median and standard deviations) were calculated from the remaining data (typically >90% of the initial burst data). Additional information that describes the burst variability and spectral data such as the root-mean-square error (RMSE) of the algorithm fit were used to flag erroneous data from the time series, resulting in the elimination of approximately 2% of the data from this record.

A regression of depth- and width-integrated discrete NO_3^- plus nitrite (NO_2^-) concentrations with sensor NO_3^- concentrations on 25 dates covering a range of flow conditions shows the two were strongly correlated (Figure 1), indicating

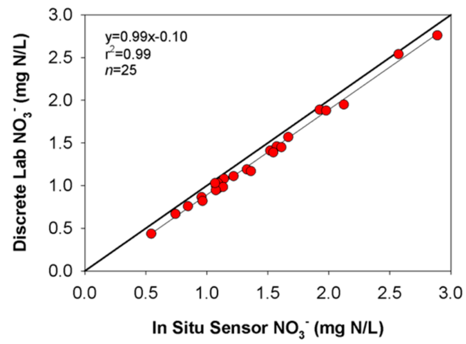

Figure 1. Relationship between in situ sensor NO_3^- concentrations and depth- and width-integrated discrete lab NO_3^- concentrations (mg N/L) in the Mississippi River at Baton Rouge (USGS gage 07374000) during the study period.

that the sensor measurements were representative of the cross-sectional averaged concentrations. However, the data showed a consistent instrument bias (overestimate) of +0.10 mg N/L that was corrected for during postprocessing as described in Pellerin et al.[17] While the SUNA does not explicitly account for absorbance by NO_2^- in the range of 210−220 nm, the concentration of NO_2^- is almost always negligible in surface waters and has little effect on reported N concentrations in the Mississippi River (Supporting Information (SI) Table SI−S1). Therefore, we hereafter refer to the sensor measurements as "NO_3^-" in units of mg N/L.

Discrete NO_3^- Measurements. Depth- and width-integrated discrete water quality samples (~12−14 per year) were collected at biweekly to bimonthly intervals approximately 150−2100 m upriver from the continuous monitoring location at Baton Rouge. Water was composited from several locations across the ~900 m cross section of the river, processed and stored at 4 °C until analyzed at the USGS National Water Quality Laboratory for nitrate plus nitrite using the enzymatic reduction method.[19] Discrete samples were also collected on adjacent days at the USGS station at St. Francisville approximately 52 km upriver (07373420), which had nearly identical NO_3^- concentrations to Baton Rouge based on the historical discrete record ($y = 0.99x + 0.0074$, $R^2 = 0.99$; $n = 120$). Previous studies have shown that NO_3^- currently makes up approximately two-thirds of the total N load from the Mississippi River, with the remaining load largely in dissolved organic form.[1,3]

Measured NO_3^- Loads. The daily NO_3^- loads (kg N/day) were calculated as a product of the daily mean NO_3^- concentration from sensor measurements and daily mean discharge. The variability in discharge and NO_3^- concentration within a day was small (mean CV = 1.6 and 1.7%, respectively),

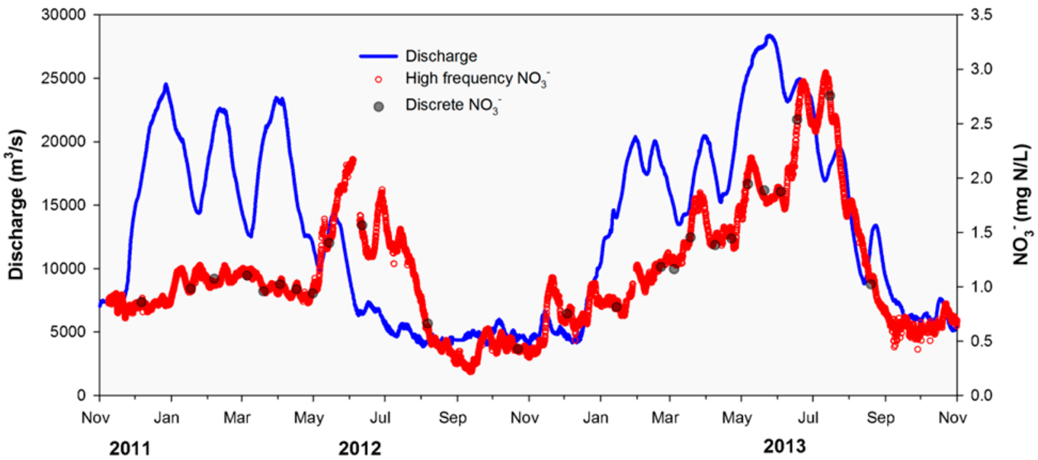

Figure 2. Time series of discharge (m^3/s) and discrete and high frequency NO_3^- concentration (mg N/L) from November 2011 to November 2013 in the Mississippi River at Baton Rouge (USGS gage 07374000).

resulting in a small percentage error that was incorporated into the load error estimates described below. The daily load was estimated for 9 days with missing NO_3^- data (of the 724 day record) based on the relationship between NO_3^- load and daily discharge on several days immediately before and after the missing values. The measured monthly loads were calculated as the sum of daily loads and were compared against modeled monthly NO_3^- loads.

Modeled NO_3^- Loads. Three regression-based models were used to estimate NO_3^- loads in the lower Mississippi River by developing a regression model against discharge, time, and other user-specified data variables. Load Estimator (LOADEST[20]) is an adjusted maximum likelihood estimator (AMLE) method that uses additional flow terms from two upstream stations (Mississippi River at Thebes and the Ohio River at Grand Chain). The composite method[21] is a hybrid approach based on the AMLE estimates but includes a routine for period-weighting residual concentrations. Additional information and monthly loads from both LOADEST and the composite method for the Mississippi River basin are described in detail by Aulenbach et al.[5] and are publically available online.[22] The Weighted Regression on Time, Discharge, and Season (WRTDS[23]) is also a regression-based approach, but it primarily differs from LOADEST and the composite method in that the model coefficients vary for every combination of discharge and time in the period of record.

Both LOADEST and the composite method were calibrated against the current and previous four years of NO_3^- data at St. Francisville and discharge from the Mississippi River at Tarbert Landing (US Army Corps of Engineers site 01100) to account for a range of flow and NO_3^- concentrations. WRTDS is intended for use with data sets of more than about 200 observations of water quality over a time span of 20 years or more,[23] and we therefore used the discrete NO_3^- record at St. Francisville from 1967 to 2013 to estimate monthly loads during the study period. All models generated mean monthly load estimates, but only LOADEST included uncertainty estimates (reported as standard errors and 95th percentile confidence intervals).

Error Estimation for Measured Loads. The error in NO_3^- sensor concentrations and loads was estimated using a root-mean-square error propagation approach[24,25] based on the following equation:

$$E_P = \sqrt{\sum (E_1^2 + E_2^2 + E_n^2)}$$

where E_p is the probability range in error, n is the total number of sources of error, and $E_1 ... E_n$ are the potential sources of error.

The potential sources of error in NO_3^- concentrations included the following: (1) sensor electronic "noise"; (2) variability in the parcel of water passing by the sensor during the burst measurement period; (3) representativeness of the sensor location in the channel; (4) deviation from validation samples (e.g., discrete lab measurements); and (5) analytical error in validation samples. Additional sources of uncertainty in the daily loads included: (6) averaging of discharge and NO_3^- concentrations to daily values; and (7) integrated uncertainty in discharge measurements. These errors were accounted for by propagating the standard error in the 30 s sensor burst measurement (excluding burst outliers) at each sampling interval (1, 2), the residual standard error in the regression between the validation (e.g., discrete) and sensor NO_3^- data (3−5), and the standard error in averaging NO_3^- concentrations over a day (6). Error in discharge measurements has not been determined for this site, but previous studies have reported a typical error of 3−6% in large rivers[26] and we use 5% as a conservative estimate. Errors were calculated as standard errors and reported here as percentage errors.

The estimated percent error in instantaneous sensor NO_3^- concentrations ranged from 1.5 to 19.7% (mean = ± 0.04 mg N/L) and was largely attributed to the standard error of the prediction between discrete laboratory NO_3^- concentrations and concurrent sensor measurements (r^2 = 0.99, slope = 1, n = 25). The error estimates for daily NO_3^- loads range from 5.2 to 20.3% per day (mean = 7.3%), with errors inversely related to discharge. The error in monthly NO_3^- loads ranged from 1.0 to 2.3% based on the daily NO_3^- loads added in quadrature (e.g., the square root of the sum of the squared daily loads) and assumed to be independent.

RESULTS AND DISCUSSION

Variability and Patterns in NO_3^- Concentrations and Loads. The NO_3^- concentrations measured in situ in the Mississippi River at Baton Range ranged from 0.22 to 2.97 mg N/L during the study period (Figure 2), spanning nearly the entire range observed in lower Mississippi River discrete samples since 1980 (0.23−3.15 mg N/L, n = 361 at St.

Francisville; Figure 3). The measured high frequency NO_3^- concentrations were typically lowest in September and highest

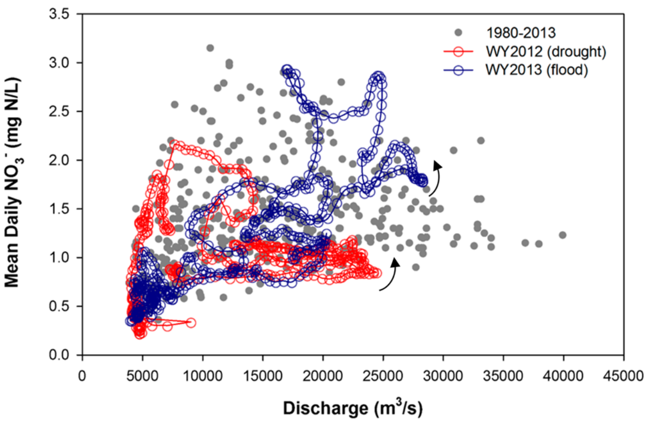

Figure 3. Relationship between mean daily discharge (m^3/s) and mean daily NO_3^- concentration (mg N/L) based on discrete data (1980−2013, n = 361) and high frequency sensor data (2011−2013). Arrows show the direction of the dominant direction in the hysteresis (counterclockwise).

in June or July, consistent with previous studies[14,27,28] and reflected the seasonality in precipitation, snowmelt runoff, fertilizer applications and relative groundwater contributions to the Mississippi River. The lowest concentration measured during the 2012 drought (0.22 mg N/L in September 2012) was similar to concentrations measured during the 1988 summer drought, suggesting that lower water depths and longer water residence times associated with droughts may increase in-stream N retention in both small headwater streams and larger tributaries.[29] The importance of N retention within the mainstem of the Mississippi River was not explicitly evaluated during this period, but other studies,[29,30] coupled with a lack of discernible diel NO_3^- variability in our data, suggests that in-stream primary production in the mainstem river is not a dominant factor influencing NO_3^- concentrations.

Despite a lack of diel patterns, the high frequency data revealed considerable variability in both NO_3^- concentrations and concentration−discharge relationships over short (e.g., days to weeks) and longer (seasons to years) time scales. For example, our data showed that NO_3^- concentration changed in the Mississippi River by more than 20% in a week without concomitant changes in discharge (Figure 4), suggesting somewhat rapid changes in the sources and processes responsible for NO_3^- transport in a large river. Establishing a relationship between NO_3^- concentration and discharge is critical to regression-based load estimation modeling, but our data showed NO_3^- concentrations varying by 2 to 3-fold across much of the hydrograph (Figure 3). This weak correlation was also evident in the historical discrete sampling record (1980−2013, Figure 3) and may be explained in part by the relative timing of runoff from the higher NO_3^- upper Mississippi River basin and the lower NO_3^- Ohio River basin.[31,32] However, an additional factor likely influencing NO_3^- concentration variability during our study was the accumulation of inorganic N in soils during the drought period and the subsequent flushing during the spring floods in 2013. This "memory effect" has been well-documented by a number of previous studies in the Mississippi River basin and is attributed to both increased storage of applied N and reductions in crop uptake and yields during droughts.[3,8,13−16]

The measured daily NO_3^- loads at Baton Rouge ranged from 0.09×10^6 to 6.1×10^6 kg N per day for the study period, with estimates of error ranging from 5.2% to 20.3% per day at high and low flows, respectively (average = 7.3%). The discharge explained 79−81% of the variability in the daily NO_3^- loads in 2012 and 2013 water years (SI Figure SI-S1), which is consistent with the results of other studies showing discharge variability as the dominant driver of NO_3^- loads in the lower Mississippi River.[13,15,16] Monthly NO_3^- loads ranged from 4.6 $\times 10^6$ to 147×10^6 kg N per month (1.0−2.3%; Figure 4), with the highest load from May to July 2013. The measured monthly NO_3^- loads were in the highest or lowest 10% of historical LOADEST monthly loads for several months during our study period (Figure 4), highlighting the extreme conditions that affected both runoff volumes and the accumulation and flushing of NO_3^- from soils as key drivers of variability in Mississippi River NO_3^- load.

Comparison of Modeled and Measured Loads. A comparison of the modeled NO_3^- loads with measured (sensor) loads across the entire study period revealed underestimates of only 3.5% for all three regression models, but much larger percentage differences at monthly time steps (Figure 5a). The absolute differences in loads (kg N/mo) were

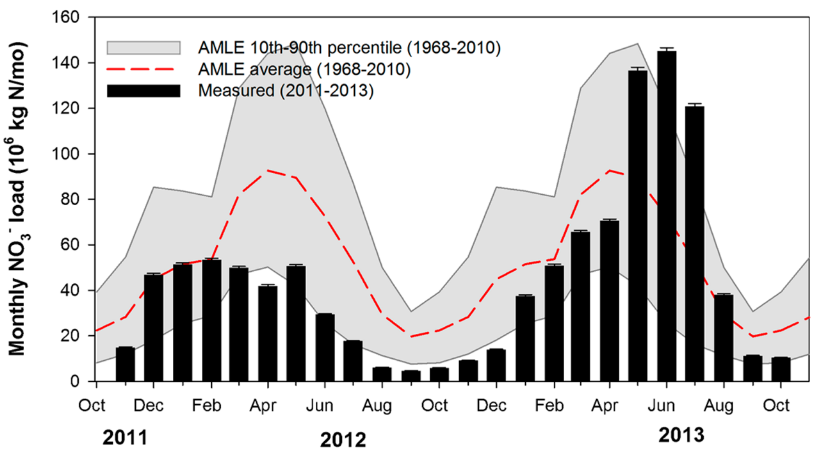

Figure 4. Monthly NO_3^- loads ($\times 10^6$ kg N) and uncertainty from sensor measured values from November 2011 to November 2013. The dashed line is the monthly LOADEST average from 1968 to 2010, and the shaded area represents the 10th and 90th percentiles over the same period.

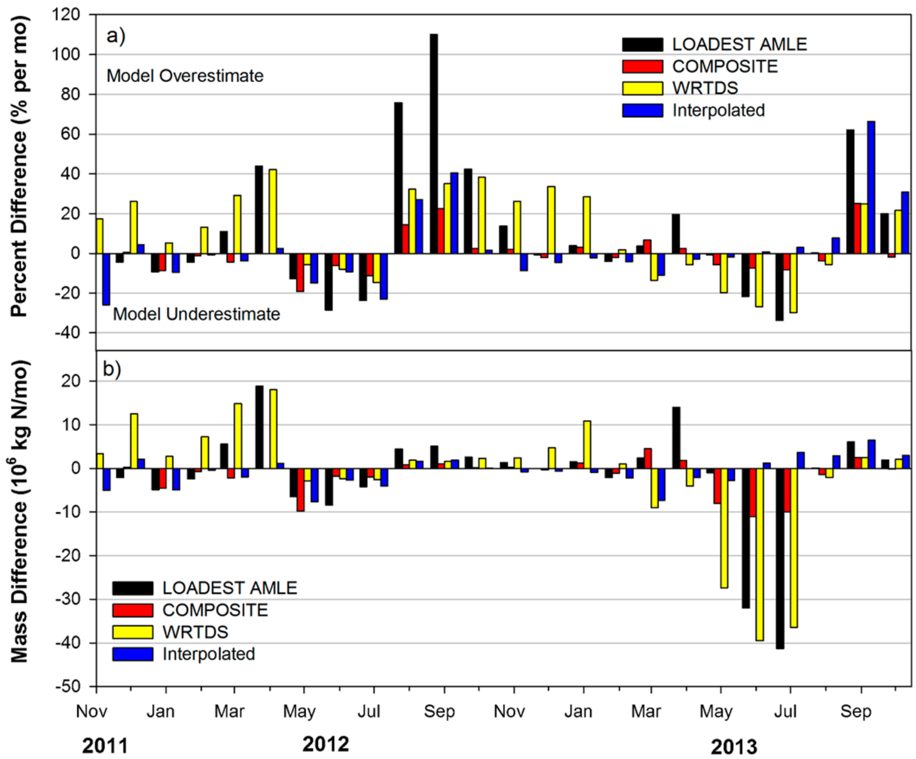

Figure 5. Difference between the modeled NO_3^- N loads (regression-based and linearly interpolated) and sensor measured NO_3^- N loads expressed as (a) a percentage deviation from measured monthly loads (%) and (b) a mass deviation from measured monthly loads ($\times 10^6$ kg N).

typically greatest during the spring and early summer (Figure 5b), with the largest load differences for all regression models during the flood period of 2013 (May to June). While a consistent bias in modeled monthly loads was not observed across the entire period, all models tended to underestimate the NO_3^- load during the spring months critical to the formation of Gulf hypoxia and overestimate loads during the rest of the year (Figure 5).

The measured spring loads (May to June) in 2012 and 2013 were in the ninth and 85th percentiles of long-term LOADEST loads near Baton Rouge, respectively (Figure 4). Such extreme dry and wet periods are typically not well-represented with historical data and can, therefore, be difficult to model with regression-based load estimation techniques.[33] For example, Murphy et al.[8] found that modeled (WRTDS) NO_3^- concentrations in the Mississippi River basin were 8−21% lower than expected when the previous year was 50% wetter than average. The large mass differences in the spring of 2013 clearly suggest the difficulty in predicting anomalously high NO_3^- concentrations following a drought. The duration of a memory effect on riverine NO_3^- loads is not known, although Raymond et al.[13] suggested that a significant fraction of fertilizer N input is transported within 24 months in average-to-wet years.

The modeled NO_3^- loads also differed from one another as has been observed for other model comparisons in the Mississippi River basin and elsewhere.[28,33−35] The composite method monthly NO_3^- loads were closest to measured loads (Figure 5), suggesting that period-weighting (e.g., adjusting the regression model predicted concentration to the observed concentration on days when samples are collected[21]) improves model accuracy during years with extreme climatic conditions. This is particularly evident during the spring flush of 2013 where composite method loads were within 8% of the measured NO_3^- loads, while LOADEST and WRTDS differed from measured monthly loads by up to −21 and −27%, respectively (Figure 5).

While Gulf hypoxia models typically use regression model output to estimate riverine N loads,[1,27,36] loads estimated from simple linear interpolation (e.g., daily discharge multiplied by the linearly interpolated daily NO_3^- concentrations between discrete samples) using seasonally weighted samples in the Mississippi River at Baton Rouge (n = 12−14 per year; Figure 2) were similar to the composite method loads and closer to measured loads than WRTDS or LOADEST for most months during our study (Figure 5). However, loads estimated by linear interpolation can be particularly sensitive to the frequency and distribution of samples,[21] while regression models such as LOADEST or WRTDS can predict loads with as few as 4−6 samples per year. Therefore, hybrid or adaptive modeling approaches that are influenced less by the timing and number of samples may become increasingly important in areas without high frequency NO_3^- monitoring given the projected changes in the intensity of precipitation and frequency of large floods in the Midwestern U.S.[37,38]

The error estimates for the measured monthly loads ranged from 1.0−2.3% and accounted for errors associated with the NO_3^- measurements as well as estimated errors in discharge (Figure 4). Of the regression models tested, error estimates are only calculated by the LOADEST model given the nature of the other two models.[5,35] Similarly, error estimates are not typically calculated with linear interpolation techniques. The LOADEST monthly load errors computed using the method of Cohn et al.[39] were reported at 8−12% during our study period, but the actual uncertainty may be higher given that errors in discharge are not included (LOADEST incorporates the standard regression assumption that all explanatory variables have zero error) and also does not include errors due to model misspecification (LOADEST incorporates the standard regression assumption that the model adequately describes the true relationship between load and the explanatory variables). Therefore, the high frequency NO_3^- measurements appear to be an effective way to improve the accuracy and reduce the uncertainty inherent in modeling NO_3^- loads to the Gulf of Mexico.

Benefits of High Frequency Measurements for Understanding and Managing NO_3^- Loads. Previous studies[33,34] have highlighted concerns over the accuracy and precision of monthly load estimates with regression-based models, which can be very sensitive to regression model misspecification and other violations of the standard regression assumptions (particularly the assumption of residual error homoscedasticity). Similarly, estimates of monthly loads using linear interpolation between discrete samples can be particularly sensitive to the timing and number of discrete samples.[21] Therefore, continuously measuring NO_3^- loads rather than modeling them offers a number of potential benefits for understanding and managing river N delivery to the Gulf.

Improved Accuracy of Monthly Loads. Improving the accuracy of monthly NO_3^- loads with high frequency measurements may be beneficial for targeting and assessing nutrient reduction strategies in the basin, as well as for refining a key input (riverine N loads) to Gulf hypoxia models. The observed differences between measured and modeled loads using regression techniques are not unexpected given the challenges of fitting linear-regression models to limited discrete data sets and across all flow conditions. However, these differences may be accentuated during extreme climatic periods—as observed during the drought-to-flood years in our study—where concentration—discharge relationships (Figure 4) are not well-represented by historical data and are particularly difficult to model.[33] The NO_3^- load estimates based on a linear interpolation of discrete concentration data may better characterize anomalies in NO_3^- concentrations than regression-based approaches, but that is entirely dependent on the frequency and distribution of discrete samples.[21]

On a per sample basis, the cost of continuous NO_3^- monitoring in a large river like the Mississippi is very small compared to discrete sample collection, which may cost up to several thousand dollars per sample when factoring in personnel, equipment and lab analyses. However, the current costs associated with purchasing and maintaining in situ NO_3^- sensors will likely limit their spatial extent on the landscape in the near future, highlighting the importance of continuing to improve the accuracy of modeled load estimates. High frequency NO_3^- measurements may help in doing so by providing temporally rich data sets that can be used to explore the correlation structure in the model error terms[40] (e.g., differences between measured and modeled values) at sites like Baton Rouge. A clearer understanding of the timing and factors resulting in model error at select sites may ultimately lead to improvements in model applications to sites without high frequency measurements.

Reduced Uncertainty in NO_3^- Loads. While reducing the uncertainty in NO_3^- loads does not directly translate into management actions, it does provide a number of important benefits for decision makers and watershed managers. For example, the small errors (±1.0−2.3%) in our monthly NO_3^- loads from high frequency measurements suggests that changes related to basin management or climate change will be easier to detect than with models that have significantly larger errors (e.g., LOADEST) or errors that cannot be quantified (WRTDS and composite method). Uncertainty in NO_3^- loads has also be shown to impact the performance of some numerical models of Gulf hypoxia,[41] although uncertainty in other input parameters such as wind speed may have equal or greater importance.

New Insights into NO_3^- Sources and Processes. High frequency NO_3^- measurements allow for a clearer picture of temporal dynamics than is possible with the current generation of regression models or period-weighted approaches. For example, high frequency data show that NO_3^- concentration can change in the Mississippi River by more than 20% in a week without concomitant changes in discharge (Figure 4), suggesting somewhat rapid changes in the sources and/or processes responsible for NO_3^- transport in a large basin. High frequency NO_3^- measurements also suggested multiple concerted flushing events in 2013 (May ninth, June 22nd and July 12th), with the peak on June 22nd resulted in a daily NO_3^- load that was within 3% of the highest daily load calculated from discrete samples (n = 361, 1980−2013) but at a discharge that was 26% lower (SI Figure SI-S1). Quantifying these dynamics at key locations in the basin and in real-time will undoubtedly yield new insights into the sources and processes controlling NO_3^- transport within the basin, as well as inform management actions targeted at reducing NO_3^- loads to the Gulf.

Implications for Gulf Hypoxia. Improved accuracy and reduced uncertainty in riverine N loads should in theory improve the ability to predict hypoxia given that riverine loads are a key input to the Gulf hypoxia models. However, the impact of variability in physical factors that affect ocean circulation can play an equally important or greater role in hypoxia formation. For example, the duration of upwelling-favorable (E-W) winds explained 32% of the observed variability in hypoxic area from 1985 to 2010 (hurricane years excluded) compared to 31% explained by May NO_3^- loads.[42] Similarly, Turner et al.[6] found that the actual size of the hypoxic zone was 68% of the predicted size during recent years where tropic storms or strong winds occurred in the Gulf just before or during the midsummer cruise (1997, 2003, 2005, and 2008−2011). Therefore, the challenges inherent in predicting hypoxia and the frequency at which these events occurred highlights a challenge that will not be alleviated with more accurate N loading, but will instead require new hydrodynamic and biogeochemical models that capture the complexities of hypoxia formation in the Gulf.[36,43]

■ ASSOCIATED CONTENT

Supporting Information

Additional information on discrete N data, NO_3^- loads by different methods and discharge—load relationships are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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