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High frequency measurement of nitrate concentration in the Lower Mississippi River, USA

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SUMMARY

Nutrient concentrations in the Mississippi River have increased dramatically since the 1950s, and high frequency measurements on nitrate concentration are required for accurate load estimations and examinations on nitrate transport and transformation processes. This three year record of high temporal resolution (every 2–3 h) data clearly illustrates the importance of high frequency sampling in improving load estimates and resolving variations in nitrate concentration with river flow and tributary inputs. Our results showed large short-term (days to weeks) variations in nitrate concentration but with no diurnal patterns. A repeatable and pronounced seasonal pattern of nitrate concentration was observed, and showed gradual increases from the lowest values in September (during base-flow), to the highest in June – which was followed by a rapid decrease. This seasonal pattern was only moderately linked with water discharge, and more controlled by nitrogen transformation/export from watershed as well as mixing patterns of the two primary tributaries (the upper Mississippi and the Ohio Rivers), which have distinctly different nitrate concentrations and flow patterns. Based on continuous *in situ* flow measurements, we estimated 554–886 × 10^6 kg of nitrate-N was exported from the Mississippi River system during years 2004–2006, which was <9% and <16% lower than U.S. Geological Survey's (USGS) estimates using their LOADEST or composite methods, respectively. USGS methods generally overestimated nitrate loads during rising stages and underestimated the loads during falling stages. While changes in nitrate concentrations in large rivers are generally not as responsive to alterations in diurnal inputs and/or watershed hydrology as small rivers, high-frequency water quality sampling would help in monitoring short-term (days to weeks) variations in nutrient concentration patterns and thus improve the accuracy of nutrient flux estimates.

1. Introduction

Historical increases in nitrate loading in the Mississippi River have been shown to be linked with increases in phytoplankton blooms (Lohrenz et al., 1997; Turner and Rabalais, 1994) and in part, hypoxia events on the Louisiana shelf (Justic et al., 1993; Rabalais et al., 2001; Turner and Rabalais, 1994). Accurate estimates of nitrate fluxes from the Mississippi River are of particular importance as they relate to watershed nitrogen budgets and biogeochemical modeling of the northern Gulf hypoxia (Mitsch et al., 2001; Scavia et al., 2003; Turner et al., 2006; Green et al., 2008). Prior studies have shown that accuracy of riverine constituent load estimates is highly dependent on sampling strategies and methods of load estimations. In streams and small rivers, greater accuracy of these estimates occurs with more frequent sampling – especially during storm events (e.g., Guo et al., 2002; Vidon et al., 2009; Bowes et al., 2009; Birgand et al., 2011). However, the effect of greater sampling frequency decreases with increasing stream order (Burt et al., 2011). An alternative to intensive monitoring involves using regressions between daily flow and constituent concentrations to estimate daily loads, and careful selection of rating curves for more accurate load estimates (Vidon et al., 2009; Birgand et al., 2011; Verma et al., 2012; Bende-Michl et al., 2013). Past nutrient measurements in the Mississippi River have been conducted at monthly intervals using several different rating curves (Goolsby et al., 1999; Runkel et al., 2004; Aulenbach and Hooper, 2006; Sprague et al., 2011). Unfortunately, there still exist large uncertainties in annual load estimates from these monthly measurements (Science Advisory Board, 2007 and references within),

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probably owing to lack of short-term observations or failure to satisfy inherent assumptions in the rating curves.

Technologies of *in situ* optical sensors/analyzers have been used worldwide to track the nitrate pulses, examine diurnal to seasonal variability of nitrate concentrations, and evaluate sampling strategies for nitrate flux estimation (Scholefield et al., 2005; Pellerin et al., 2009, 2012; Bark, 2010; Rusjan and Mikoš, 2010; Ferrant et al., 2012). High-frequency chemical monitoring in small rivers has shed new light on hydrochemical evolution in catchment basins and streams, and yielded new insights for testing hydrological models (Kirchner et al., 2004; Moraetis et al., 2010; Bende-Michl et al., 2013). Until now, no such high-frequency monitoring data have been reported for large rivers such as the Lower Mississippi River (LMR). Prior studies on the LMR (Turner and Rabalais, 1991; Lohrenz et al., 1997; Duan and Bianchi, 2006; Duan et al., 2010; Sprague et al., 2011) have shown pronounced temporal variability in nitrate concentrations since the early 20th century. While much of this temporal variability has been attributed to changes in land-use and chemical fertilizer inputs (Turner and Rabalais, 1991), detailed hydrological and biogeochemical dynamics of these changes still remain poorly understood. These processes may include "dilution" by stormwater, recycling of point and nonpoint N in watershed soils, N "spiraling" in streams and river networks (Ensign and Doyle, 2006), and N removal via denitrification (Richardson et al., 2004). Here we posit that more frequent temporal measurements of nitrate concentration are needed in the LMR to better understand nitrate transport and transformation in the river, as well as sporadic changes in blooms and hypoxia on the Louisiana shelf (e.g., Bianchi et al., 2010).

In recent years, supported by the U.S. Geological Survey (USGS) National Stream Quality Accounting Network, Cooperative Water Program, and the National Water-Quality Assessment Program, the cutting-edge technologies of *in situ* optical sensors are being used at 36 sites in the Mississippi River basin, including the LMR near Baton Rouge (Louisiana) and several large tributaries to the river (the Missouri River, Ohio River, Illinois River, and Iowa River), providing new opportunities for researchers to better study the storage and transport of nitrate from headwaters to the Gulf of Mexico (http://www.usgs.gov/newsroom/article.asp?ID=3668, access September 2013). Preliminary data from the Upper Mississippi River (UMR) Navigation Pools and a tributary (Raccoon River) have shown that diurnal and seasonal patterns of nitrate concentration can be tractable with *in situ* nitrate sensors (Bark, 2010). In this paper, we present for the first time, high resolution data of nitrate concentrations in the LMR, using an *in situ* nitrate analyzer that was deployed for a period of ca. three years (June 2003–September 2006). The objectives of this study were to better estimate annual nitrate fluxes from the Mississippi River to the Gulf coasts, make comparisons with prior flux estimates for method improvements, and evaluate sampling frequency of *in situ* measurements in large rivers. In order to interpret temporal patterns of nitrate concentration in the LMR, we estimated daily nitrate inputs from four primary tributaries (UMR, Missouri River, Ohio River, and Arkansas River) from U.S. Geological Survey (USGS) historical data, and calculated daily contributions from these primary tributaries to nitrate in the LMR. We hypothesized that, (1) diurnal nitrate patterns in the LMR will not be as apparent as in small rivers owing to less connectivity to the watershed and less *in situ* transformations in large rivers, and (2) monthly to seasonal variability of nitrate concentrations will be largely attributed to conservative water mixing of primary tributaries, which differ in river flow pattern and nitrate level. The results from this work have implications for how river systems can be better managed in an attempt to reduce the seasonal hypoxia, in the near-field regions (in the particle plumes) of the Mississippi/Atchafalaya plumes on the inner Louisiana shelf.

2. Material and methods

2.1. Study site

The Mississippi River is the largest river system in North America which drains an area of 3.22×10^6 km^2, nearly 40% of the landmass of the contiguous United States. The Mississippi River is the dominant source of freshwater, sediment, terrestrial organic carbon and nutrients to the northern Gulf of Mexico (Bianchi et al., 1999; Milliman and Farnsworth, 2011). The three tributaries of the river (upper Mississippi, Missouri and Ohio; Fig. 1) are the primary contributor for nutrient, sediment and water, respectively (Turner et al., 2007). In the LMR (the section below its confluence with the Ohio River to Head of Passes), approximately one third of the river discharge is diverted to the Atchafalaya and Wax Lake outflows via the Old River Control Structures (ORCS; Dagg et al., 2007). Below the ORCS, the LMR flows through Baton Rouge and New Orleans to Head of Passes, and is constrained throughout by earthen levees and dikes (built with sediments on a cleared and leveled surfaces) in this section (Allison et al., 2012). In order to take advantage of existing structures in the river and to ensure easy access to the equipment, the site of this study was located on a floating dock near the U.S. Army Corps of Engineers Carrollton Station (river kilometer 166 or RK166), within a straight stretch of the river in New Orleans, Louisiana (Fig. 1). Prior work (Dagg et al., 2005) has shown there is little change in the nutrient concentrations in this stretch of the LMR. Therefore, we assumed that this station could be used as a representative location of the LMR just prior to discharge to the coastal zone.

2.2. Nitrate analyzer installation, maintenance and calibration

An Envirotech NAS 3 nitrate analyzer was installed using custom stainless-steel and aluminum tube brackets with a clamp system, welded to a floating dock, and maintained at approximately 1 m below the surface. Power of the nitrate analyzer was supplied by a deep cycle 12 V battery placed on the dock. Data were stored in the instrument until retrieval, as well as being transmitted to a Campbell Scientific CR-10 data logger, which was accessed daily via the internet to check for instrumental or power failures.

A standard wet chemistry method for brackish waters provided by Envirotech was employed for the *in situ* analyzer, as previously summarized by Sigleo et al. (2005) and Wright et al. (1997). The only instrument modification was to use a much larger filter on the intake to better contend with the high suspended sediment loads in the river (Turner et al., 2007). The instrument was programmed to collect and analyze a sample every 2 or 3 h depending upon the planned deployment duration. A 100 μM (or 1.4 mgN L^{-1}) nitrate on-board standard (OBS) was analyzed every five samples (10–15 h). This was used to compensate for instrumental drift over the course of a deployment and to detect potential problems with reagents. Even though samples were filtered at the instrument inlet, instrumental blanks (analysis of sample water without the colorimetric reagent) were performed on every sample in order to account for any particle effects on the transmittance reading. For analysis, nitrate was reduced to nitrite by pumping the sample in-and-out a cadmium tube several times. Thus, these analyses represent nitrate plus nitrite; however, nitrite generally represented less than 1% of the total inorganic N in the river (unpublished data). So, here we used nitrate plus nitrite in our estimate of nitrate. Colorimetric analyses were accomplished by complexation with sufanilamide and *N*-1-napthylenediamine. Nitrate is reported as nitrogen (e.g., mgN L^{-1}) throughout the paper.

Discrete samples were collected at each recovery/deployment and immediately filtered (0.2 μm polysulfone membrane) using a