National Stream Quality Accounting Network

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Scientific Investigations Report 2014–5100

U.S. Department of the Interior
U.S. Geological Survey

Cover. Mississippi River from the visitor's center at Vicksburg, Mississippi in May 2011, facing west. Photo credit, Claire Rose, U.S. Geological Survey.

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ton (t)	0.9072	metric ton

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

AIC	Akaike Information Criterion
AMLE	adjusted maximum likelihood estimate
DAR	deethylatrazine to atrazine ratio
DO	dissolved oxygen
LOADEST	Load Estimator
NASQAN	National Stream Quality Accounting Network
NWQL	National Water Quality Laboratory
USGS	U.S. Geological Survey

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Abstract

High streamflow associated with the April–July 2011 Mississippi River flood forced the simultaneous opening of the three major flood-control structures in the lower Mississippi-Atchafalaya River subbasin for the first time in history in order to manage the amount of water moving through the system. The U.S. Geological Survey (USGS) collected samples for analysis of field properties, suspended-sediment concentration, particle-size, total nitrogen, nitrate plus nitrite, total phosphorus, orthophosphate, and up to 136 pesticides at 11 water-quality stations and 2 flood-control structures in the lower Mississippi-Atchafalaya River subbasin from just above the confluence of the upper Mississippi and Ohio Rivers downstream from April through July 2011. Monthly fluxes of suspended sediment, suspended sand, total nitrogen, nitrate plus nitrite, total phosphorus, orthophosphate, atrazine, simazine, metolachlor, and acetochlor were estimated at 9 stations and 2 flood-control structures during the flood period.

Although concentrations during the 2011 flood were within the range of what has been observed historically, concentrations decreased during peak streamflow on the lower Mississippi River. Prior to the 2011 flood, high concentrations of suspended sediment and nitrate were observed in March 2011 at stations downstream of the confluence of the upper Mississippi and Ohio Rivers, which probably resulted in a loss of available material for movement during the flood. In addition, the major contributor of streamflow to the lower Mississippi-Atchafalaya River subbasin during April and May was the Ohio River, whose water contained lower concentrations of suspended sediment, pesticides, and nutrients than water from the upper Mississippi River. Estimated fluxes for the 4-month flood period were still quite high and contributed approximately 50 percent of the estimated annual suspended sediment, nitrate, and total phosphorus fluxes in 2011; the largest fluxes were estimated at the water-quality station located at Vicksburg, Mississippi.

The majority of the suspended-sediment flux introduced into the lower Mississippi-Atchafalaya River subbasin during the 2011 flood was in the form of fine-grained particles from the upper Mississippi River—77 percent of the suspended-sediment flux compared to 23 percent from the Ohio River. As water moved downstream along the lower Mississippi River, there were losses in suspended-sediment flux because of deposition and backwater areas. Fluxes showed a greater response to increased streamflow in the Atchafalaya River than in the lower Mississippi River. The result was a gain in suspended-sediment flux with distance downstream in the Atchafalaya River because of resuspension of previously deposited materials—particularly sand particles. Overall, 13 percent less suspended sediment left the lower Mississippi-Atchafalaya River subbasin than entered it from the confluence of the upper Mississippi and Ohio Rivers during the flood. The loss in suspended-sediment flux during the flood accounted for 14 percent of the 2011 annual suspended-sediment flux loss within the lower Mississippi-Atchafalaya River subbasin.

Nitrate composed approximately 70 percent of the total nitrogen flux at all of the sampled water-quality stations, excluding the Arkansas River. Almost 2.4 times more nitrate flux entered the lower Mississippi-Atchafalaya River subbasin from the upper Mississippi River than from the Ohio River. As nitrate moved down the lower Mississippi River and the Atchafalaya River, there were no substantial losses or gains in flux, indicating that nitrate moved conservatively within the subbasin during the 2011 flood. Although streamflow was the largest on record, nitrate flux during the flood period resulted in a zone of hypoxia in the Gulf of Mexico that was only the tenth largest on record.

The flux of total phosphorus in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood was strongly related to suspended-sediment flux at most of the stations. There were significant gains in total phosphorus flux in the Atchafalaya River during the flood period and losses between the stations along the lower Mississippi River. Overall, however, the amount of total phosphorus flux that left the lower Mississippi-Atchafalaya River subbasin was only 1.7 percent less than the flux that entered it from the upper Mississippi

River and the Ohio River, indicating that total phosphorus flux within the subbasin during the flood was conservative.

As streamflow was decreasing within the lower Mississippi-Atchafalaya River subbasin, orthophosphate composed an increasing percentage of the total phosphorus concentration, probably because of the return of waters low in oxygen concentration from areas such as inundated lands, backwater streams, and floodways. Poorly oxygenated waters promote the release of sediment-bound phosphorus into the more-readily available dissolved form (measured as orthophosphate in this study). Because of processing within the subbasin during the flood period, there was a 25-percent gain in orthophosphate flux between the confluence of the upper Mississippi and Ohio Rivers and the outlet of the subbasin.

Of the 136 pesticide compounds and degradates that were analyzed, only 18 were detected above the method reporting level. The 18 compounds that were detected fell into three categories: (1) compounds that were frequently detected and showed a response in concentration to the flood; (2) compounds that were detected in almost every sample at every station but at low concentrations; and (3) compounds that were infrequently detected. Fluxes for the most frequently detected pesticides having the highest concentrations (atrazine, metolachlor, acetochlor, and simazine) were within the low-to-middle range of historic fluxes.

An average of 66,450 cubic feet per second of streamflow was diverted from the lower Mississippi River through the Morganza Floodway into the Atchafalaya River from May 14 through July 7, 2011. Dissolved oxygen concentrations in the floodway decreased with the amount of time that the flood-control structure was open, which affected nitrate and orthophosphate concentrations. As dissolved oxygen concentrations decreased in the floodway, nitrate concentrations decreased and orthophosphate concentrations increased. Oil and gas samples were also collected at 1 station upstream and 1 station downstream from the outlet of the Morganza Floodway into the Atchafalaya River. There were no detections of petroleum hydrocarbons in the upstream or downstream samples. All concentrations of oil and grease were relatively low, and the effect of water from the floodway on water quality in the Atchafalaya River could not be determined because oil and grease samples were not collected from the floodway.

Introduction

Extreme hydrologic events, such as floods, can overwhelm the ability of a surface-water system to assimilate agricultural chemicals (nutrients and pesticides) and can transport these chemicals, along with large amounts of sediment, downstream to larger surface-water bodies. In April and May 2011, parts of the Mississippi River Basin (fig. 1) received over five times the average annual precipitation (Vining and others, 2013). When combined with snow-melt from the upper Mississippi River subbasin, streamflow on the lower Mississippi River reached historic flood levels and portions of the lower Mississippi-Atchafalaya River subbasin remained above flood stage for 2½ to 3 months. This flooding occurred during the period when agricultural chemicals had recently been applied to fields that had recently been tilled, leaving the land susceptible to overland runoff of chemicals and sediment.

The transport of pesticides and nutrients from agricultural fields into receiving surface-water bodies has been widely documented (Pereira and Rostad, 1990; Goolsby and others, 1993b; Pereira and Hostettler, 1993; Meade, 1995; Goolsby and Battaglin, 1997; Rostad, 1997; Thurman and others, 1991; Battaglin and others, 2011). Alexander and others (2008) identified nine States that contribute the bulk of nitrogen and phosphorus to the Mississippi River: Arkansas, Illinois, Indiana, Iowa, Kentucky, Mississippi, Missouri, Ohio, and Tennessee, whereas the majority of herbicides and degradation products that move into the Mississippi River have been attributed to the Missouri, Illinois, and Ohio Rivers (Pereira and Rostad, 1990). Concentrations and fluxes of pesticides and nutrients in the Mississippi River generally are highest in the spring and summer when pesticides and fertilizers are typically applied and when streamflow is highest, and then decrease substantially in the fall and winter (Pereira and Rostad, 1990; Meade, 1995; Goolsby and Battaglin, 1997). When flood events occur, concentrations of agricultural chemicals vary little from average, but fluxes increase sharply because of the increase in streamflow. For example, Goolsby and others (1993a) found a 112-percent increase in nitrate flux and a 235-percent increase in atrazine flux at the mouth of the Mississippi River during the 1993 flood, although concentrations in the Mississippi River during this time were similar to previous years.

In general, concentrations of suspended sediment peak near the beginning of a flood and then decrease as sediment supply becomes depleted (Rostad, 1997). Large amounts of in-channel bed sediments are moved during flood events, which lead to a reduction in subsequent annual suspended-sediment fluxes in large rivers (Horowitz, 2010). When suspended-sediment fluxes increase, agricultural chemicals attached to sediment can be readily transported downstream and may further exacerbate water-quality problems in receiving surface-water bodies. Horowitz (2010) estimated that suspended sediment in the Mississippi River Basin delivers about 85 percent of the annual phosphorus flux and 30 percent of the annual nitrogen flux to the northern Gulf of Mexico.

Since at least 1980, a hypoxic zone (defined as water containing <2 milligrams per liter (mg/L) of dissolved oxygen) has formed during the spring and summer in the Gulf of Mexico off the coast of Louisiana. The zone has increased in size since measurements began in the early 1980s, and its extent is positively related to the annual amount of nitrogen entering the Gulf from the Mississippi River (Rabalais and others, 2002). More recently, models have indicated that there is also a positive correlation between phosphorus transport (flux) to the Gulf of Mexico and the size of the zone of hypoxia (Scavia and others, 2004; Donner and Scavia, 2007; Scavia and Donnelly, 2007; Turner and others, 2008; Boesch

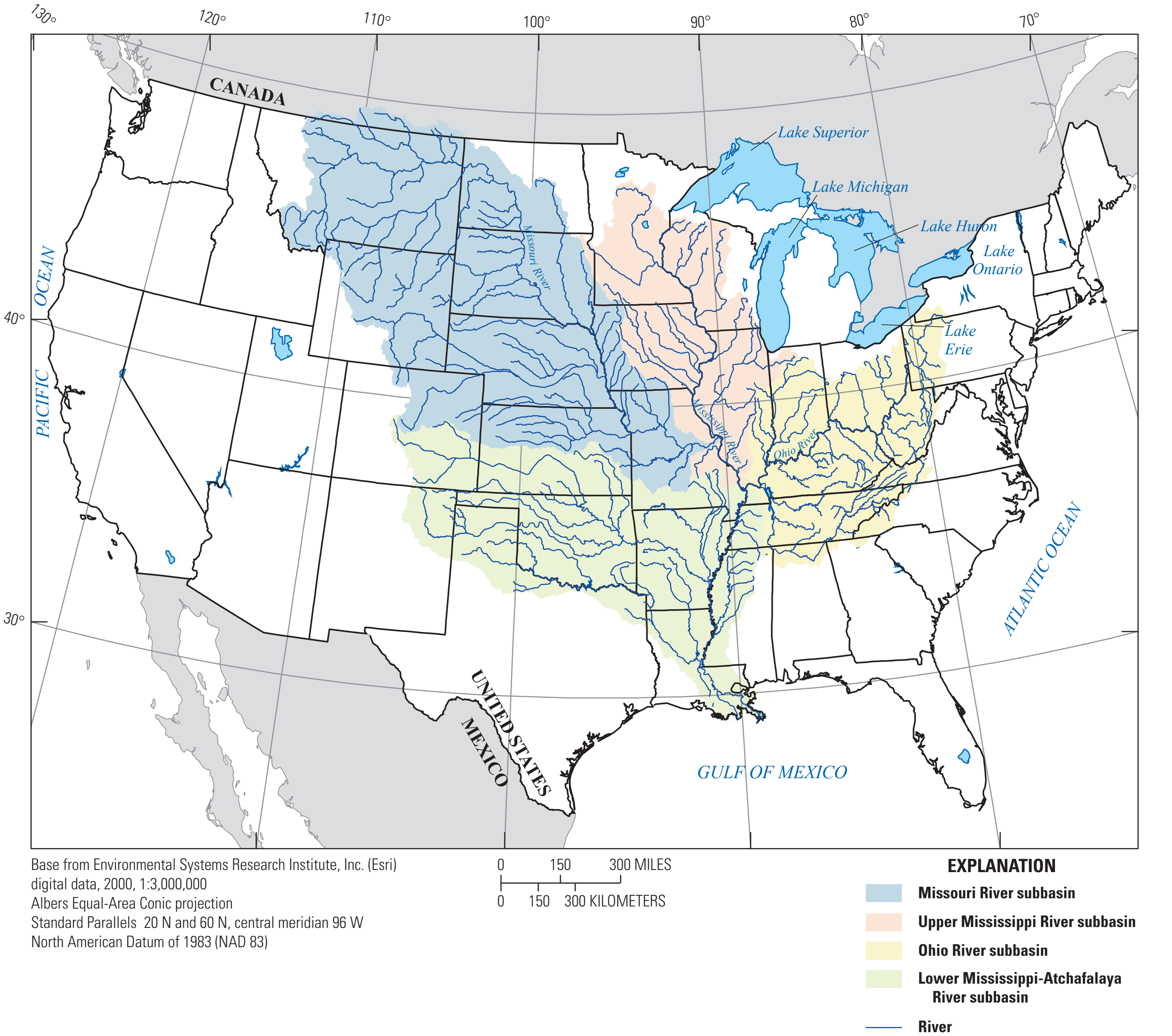

Figure 1. Extent of the Mississippi River Basin and subbasins.

and others, 2009). Although water-quality effects of floods, such as the flood during the summer of 1993, in the upper Mississippi River subbasin have been investigated (Goolsby and others, 1993a; Taylor and others, 1994; Holmes, 1996; Schalk and others, 1998; Horowitz, 2010), few studies have investigated water-quality effects in the lower Mississippi-Atchafalaya River subbasin.

The U.S. Geological Survey (USGS) has been reporting the annual and monthly flux of nutrients into the Gulf of Mexico each year at selected locations (Aulenbach and others, 2007; U.S. Geological Survey, 2009). These data have been used extensively by researchers interested in understanding the formation of hypoxia in the Gulf of Mexico (Goolsby and others, 1999; Rabalais and others, 1999; Goolsby and Battaglin, 2001; Scavia and others, 2004; Booth and Campbell, 2007; Donner and Scavia, 2007; Turner and others, 2008) and currently provide the foundation for many management decisions related to the hypoxia problem (Committee on Environment and Natural Resources, 2000, 2003; Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001, 2004; U.S. Environmental Protection Agency, 2008). An expected increase in nutrient and sediment fluxes in response to flood events, particularly during the spring, could lead to a larger than normal areal extent of the hypoxic zone.

From April through July 2011, the USGS collected water-quality samples at existing National Stream Quality Accounting Network (NASQAN) stations and selected additional sampling locations to determine the effects of the 2011 Mississippi

River flood on water quality in the lower Mississippi-Atchafalaya River subbasin. Data from this study allowed the USGS to identify two things: (1) whether sampling the existing NASQAN water-quality stations was adequate enough to characterize water quality during high-flow events and (2) whether sampling the existing water-quality stations would allow the USGS to evaluate changes in water quality in the lower Mississippi-Atchafalaya River subbasin caused by opening the flood-control structures.

Purpose and Scope

The purpose of this report is to present and summarize information on the concentrations and transport of sediment, nutrients, and pesticides in the lower Mississippi-Atchafalaya River subbasin during the April–July 2011 flood on the Mississippi River, hereafter referred to as the "2011 flood." This 4-month period includes observations made before, during, and after the peak streamflow of the 2011 flood, which occurred in May 2011. Various constituents and fluxes are discussed for 2 stations above the confluence of the upper Mississippi and the Ohio Rivers and for 9 water-quality stations and 2 flood-control structures in the lower Mississippi-Atchafalaya River subbasin for the 2011 flood (April– July 2011). Constituent concentrations and fluxes are compared to historical data collected by the USGS.

Environmental Setting

The Mississippi River originates in Lake Itasca, Minnesota, and flows over 2,340 miles (mi) through the middle United States before it empties into the Gulf of Mexico (fig. 1). The river and its tributaries drain all or part of 31 states (41 percent of the conterminous United States) from a basin area of approximately 1.245 million square miles (mi^2). The Mississippi River Basin is the largest river basin in North America and the third largest river basin in the world, smaller only than the Amazon and Congo River Basins. A large population of the United States uses the river for municipal, industrial, agricultural, and recreational purposes; about 23 percent of the public surface-water supply in the United States is from the Mississippi River and its tributaries (Pereira and Hostettler, 1993). In addition, the majority of corn, soybeans, wheat, cattle, hogs, and to a lesser extent, cotton and rice are produced from regions that are farmed within the basin. Large inputs of nitrogen from agriculture, atmospheric deposition, and point sources occur annually in the basin, especially in Minnesota, Iowa, Illinois, Indiana, and Ohio. Nutrients and pesticides applied for improved agricultural production, along with sediment from agricultural fields, can be transported via rainfall runoff and groundwater discharge into streams that eventually flow into the Mississippi River and ultimately into the Gulf of Mexico.

The lower Mississippi-Atchafalaya River subbasin is a relatively flat plain with rich, productive soils that are used extensively for agriculture. Many tributaries, such as the White River, Arkansas River, Yazoo River, and Big Black River, contribute to streamflow in the lower part of the Mississippi River Basin (fig. 2). Only 75 percent of the Mississippi River streamflow enters the northern Gulf of Mexico through the river's delta (Horowitz, 2010). The remaining streamflow is diverted by the Old River Control Structure downstream from Vicksburg, Mississippi (Miss.) where it merges with the Red River to form the Atchafalaya River about 25 mi upstream from Melville, Louisiana (La.) (Meade, 1995; Mossa, 1996).

In order to protect the alluvial plain from rising flood waters, the U.S. Army Corps of Engineers developed the Mississippi River and Tributaries Project in response to the Great Flood of 1927 (U.S. Army Corps of Engineers, 2004; Mississippi River Commission, 2008). The project consists of four major elements: (1) levees to contain flow; (2) floodways for the passage of excess streamflow past critical reaches of the river; (3) channel improvement and stabilization; and (4) tributary basin improvements (U.S. Army Corps of Engineers, 2004). The three major flood-control structures constructed as part of the project are the Birds Point-New Madrid Floodway in Missouri and the Morganza Floodway and Bonnet Carré Spillway in Louisiana (fig. 2). The 2011 flood marked the first time in history that the three major flood-control structures were operated simultaneously (Anderson, 2011). On May 2, 2011, the Birds Point-New Madrid Floodway was activated, followed by the opening of the Bonnet Carré Spillway on May 9, 2011. Opening the Bonnet Carré Spillway allowed river flows to remain under approximately 1.25 million cubic feet per second (ft^3/s), which was imperative because exceeding this threshold would have caused devastating damage to New Orleans, La., from flood waters (Anderson, 2011). The Morganza Floodway was opened on May 14, 2011, when streamflows in the Mississippi River reached approximately 1.5 million ft^3/s (Anderson, 2011), and this floodway remained open through July 7, 2011.

Methods

Sample Collection, Processing, and Analysis

Water-quality samples are typically collected 12 to 14 times per year at USGS stations that are part of NASQAN, a large-river sampling network. During the 2011 flood, the frequency of sample collection was increased to monitor the effects of the high-flow event at 2 stations above the confluence of the upper Mississippi and Ohio Rivers and 9 water-quality stations in the lower Mississippi-Atchafalaya River subbasin. For this study, the two stations located above the confluence are considered to be part of the lower Mississippi-Atchafalaya River subbasin. Samples were collected every other week in April, then weekly from the second week in May through the end of June, and every other week in July, for a total of 12 samples per site (station numbers 5, 6, and

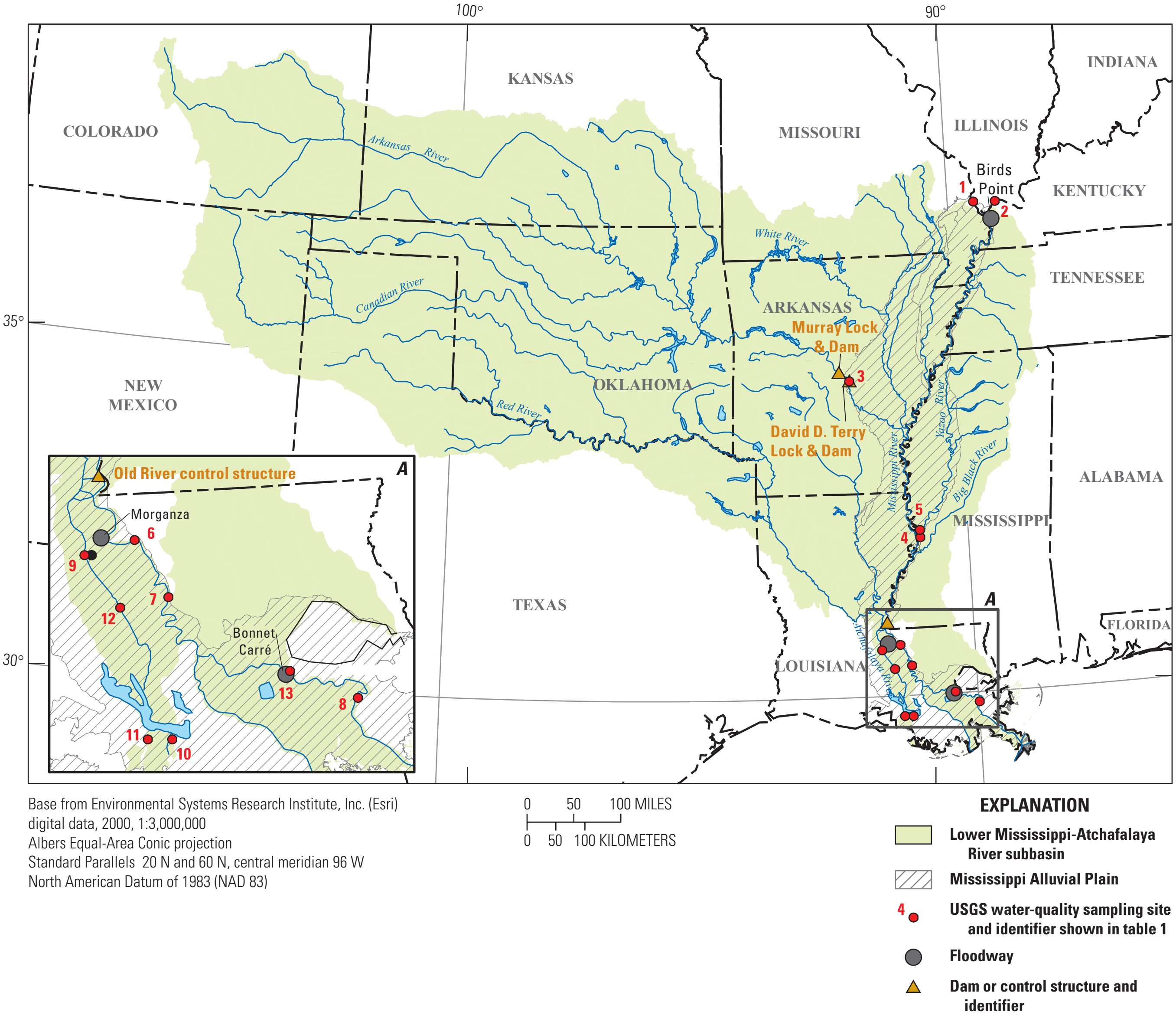

Figure 2. Lower Mississippi-Atchafalaya River subbasin and sites sampled during the 2011 flood.

8–11; fig. 2; table 1). Exceptions to this sampling protocol were made for station number 7 (sampled every other week from April through June for a total of 6 samples); station number 4 (1 sample in April and 3 samples each in May, June, and July for a total of 10 samples); station number 3 (1 sample in April, 3 samples in May and 1 sample in June for a total of 5 samples); station number 2 (4 samples in May and 2 samples in June); and station number 1 (sampled every other week from April through June and monthly in July for a total of 7 samples). Welch and Barnes (2013) lists the compounds analyzed and describes the processing and analysis for all samples collected at the water-quality stations during the 2011 flood. Data for water-quality station numbers 3 and 4 are not shown in this report, but the full dataset is provided in Welch and Barnes (2013).

Water-quality samples were collected in the Morganza Floodway (station number 12, a total of 6 water-quality samples) and in the Bonnet Carré Spillway (station number 13, a total of 7 samples). Streamflow was measured and sediment samples were collected in the Morganza Floodway at a location different from the water-quality sampling station (Morganza Spillway at U.S. Highway 190 near Lottie, La.). At the Lottie, La. location, streamflow was measured daily from May 14 through June 27, and sediment samples were collected daily from May 18 through June 10 (table 1; Welch and Barnes, 2013). At station number 13, 28 sediment samples were collected in May and June. At water-quality station numbers 9 and 10, a total of 14 samples for oil and gasoline analysis were collected (7 samples at each site in May and June (fig. 2)).

Table 1. Water-quality stations sampled in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July, and summary statistics for suspended sediment and percent sand.

[Suspended-sediment concentrations are in milligrams per liter (mg/L). USGS, U.S. Geological Survey; mi^2, square mile; N, number of samples; Min, minimum; Max, maximum; Med, median; --, not available]

Water-quality station number	USGS station name	USGS station number	Drainage area (mi^2)	Suspended sediment concentration				Percent sand			
				N	Min	Max	Med	N	Min	Max	Med
1	Mississippi River at Thebes, Illinois (Upper Mississippi River)	07022000	713,200	7	127	448	317	8	6	45	13
2	Ohio River at Dam 53 near Grand Chain, Illinois[a] (Ohio River)	03612500	203,100	7	30	109	96	6	0	18	3
3	Arkansas River at David D Terry Lock and Dam below Little Rock, Arkansas[b]	07263620	158,429	5	12	303	38	5	2	75	10
4	Yazoo River below Steele Bayou near Long Lake, Mississippi	07288955	13,355	10	9	83	33	6	0	3	0
5	Mississippi River above Vicksburg at mile 438, Mississippi[c]	322023090544500	1,144,500	12	63	164	122	12	11	57	26
6	Mississippi River near St. Francisville, Louisiana[d]	07373420	1,125,300	12	46	179	83	10	12	50	26.5
7	Mississippi River at Baton Rouge, Louisiana	07374000	1,125,800	6	88	168	134	6	11	63	56.5
8	Mississippi River at Belle Chasse, Louisiana	07374525	1,130,000	12	114	206	135	11	2	40	34
9	Atchafalaya River at Melville, Louisiana[e]	07381495	93,316	12	70	261	144	10	3	61	20
10	Lower Atchafalaya River at Morgan City, Louisiana	07381600	--	12	76	338	133	11	1	53	25
11	Wax Lake Outlet at Calumet, Louisiana	07381590	--	12	94	262	143	11	2	34	23
12	Atchafalaya Floodway near Ramah, Louisiana North of I–10[f] (Morganza Floodway)	302410091305201	--	24	8	31	16.5	24	0	14	0.5
13	Bonnet Carré Spillway at US Hwy #61near Norco, Louisiana (Bonnet Carré Spillway)	300115090245000	--	28	43	133	111	28	1	13	6

[a]Flow from the Ohio River at Metropolis, Illinois (03611500).

[b]Flow from the Arkansas River at Murray Dam near Little Rock, Arkansas (07263450).

[c]Flow from the Mississippi River at Vicksburg (07289000).

[d]Flow from the Mississippi River at Tarbert Landing, Mississippi (U.S. Army Corps of Engineers site 01100).

[e]Flow from the Atchafalaya River at Simmesport, Louisiana (U.S. Army Corps of Engineers site 03045).

[f]Flow from the Morganza Spillway at Hwy 190 near Lottie, Louisiana (07381530).

The acoustic Doppler current profiler method described by Olson and Norris (2007) was used by the USGS to measure instantaneous streamflow at the sampled stations, where streamflow is the volume of water moving down a stream or river per unit of time, measured in cubic feet per second. At six stations (station numbers 2, 3, 5, 6, 9, and 12; fig. 2; table 1), instantaneous streamflow was measured at a separate location from where the water-quality sample was collected. The mean daily streamflow (Q) was calculated and reported by the USGS according to standard procedures (Rantz, 1982). The U.S. Army Corps of Engineers monitored daily streamflow at the Mississippi River at Tarbert Landing, Miss., (associated with water-quality station number 6), total outflow at the Old River outflow channel near Knox Landing, La., (shown as the Old River Control Structure on fig. 2), and streamflow at the Atchafalaya River at Simmesport, La., (associated with station number 9; fig. 2; table 1).

Laboratory Data Analysis

Some concentrations of pesticides and hydrocarbons were estimated by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, and TestAmerica Laboratories, Inc., in Arvada, California, respectively, and were denoted with an "E". Values with a remark code of "E" were treated as detections in this study unless the value was lower than the method reporting level for that constituent. All detected values lower than an established method reporting level were "censored" and reported as less than (<) the method reporting level.

Water-Quality Dataset Preparation

The protocols for preparing the water-quality dataset and screening for outliers were similar to those of Aulenbach and others (2007). A change was made to these protocols for days with multiple samples. In lieu of averaging all sample concentrations collected during a given day (including replicates), the concentration from the routinely collected sample was used.

Flux Estimation Methods

Streamwater constituent load, also known as mass flux, is the mass of chemical constituent or sediment transported past a point in a stream over a given period of time. Flux (Φ) is the product of constituent concentration (*C*) and streamflow (*Q*), integrated over time (*t*):

$$\Phi = \int C(t)Q(t)dt \,. \qquad (1)$$

Flux calculations using the integral in equation 1 require a continuous record of concentration and streamflow. Although streamflow can be measured at a sufficiently high frequency, constituent concentration typically is measured less frequently because of the effort required to collect and analyze water-quality samples. Several flux estimation approaches have been proposed to address the issue of using only discrete sample concentrations. In this report, three different approaches are used to estimate concentrations continuously throughout the flux estimation period: a period-weighted approach, a regression-model method, and the composite method (a hybrid method incorporating both the regression-model and period-weighted approaches). All approaches were not applied at all sampling locations and different approaches were necessary because of differences in (1) sampling frequencies, (2) sampling periods, and (3) the strength of the relation between concentration and streamflow and whether it was sufficient to use in a regression model to estimate concentrations through time. The methodology of the three flux estimation approaches are described next, followed by specifics regarding which methods were implemented at each of the sampling locations.

A period-weighted approach is a flux estimation method in which measured concentrations are assumed to represent the periods when the samples are collected. In this study, a continuous, daily streamwater-concentration series was developed for days without samples by linearly interpolating sample concentrations (through time) between days with samples (Larson and others, 1995). The product of this piecewise linear function of concentration and daily average streamflow is summed through time to estimate flux. This flux estimation approach is sensitive to sampling frequency and the distribution of sampling through hydrologic events, which can result in bias. There is also no direct way to estimate the degree of uncertainty in the flux estimates. Although the regression-model method is often preferred, a period-weighted approach is useful in situations where the following three criteria are satisfied: sampling is insufficient to model concentrations, the relation between measured concentrations and other variables is not strong enough to develop a predictive model of concentration, and samples are collected at a sufficient frequency to provide strong serial correlation between sample concentrations. Streamflow, and hence, water-quality sampling, occurred at several stations only during the 2011 flood, so although samples were collected fairly frequently during the flood, the overall number of samples collected at these stations is quite low. This resulted in a number of cases in which the number of samples was insufficient to develop a regression model but the frequency of sampling was sufficient to apply a period-weighted approach.

The second approach employed to estimate flux in this study is the regression-model method, also known as the rating-curve method, which is a standard statistical technique that can be used to estimate concentration continuously, thus enabling a direct calculation of mass flux. This method uses a regression model relating concentration (or flux) to continuous variables, such as streamflow and Julian day of year (for example, Johnson, 1979; Cohn and others, 1992). Fluxes were estimated as a function of a second-order polynomial of average daily streamflow, a second-order polynomial of time (for long-term trends), and a pair of sinusoidal seasonal terms using a seven-parameter regression-model equation of the form

$$\ln(L_i) = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi\ dtime) + a_4 \cos(2\pi\ dtime) + a_5\ dtime + a_6\ dtime^2 + \varepsilon, \quad (2)$$

where

- ln is the natural logarithm (log base e);
- L_i is the calculated load for sample i;
- $\ln Q$ is ln (daily average streamflow) minus center of ln (daily average streamflow);
- *dtime* is decimal time minus center of decimal time (as defined by Cohn and others, 1992);
- ε is error; and
- $a_0 ... a_6$ are the fitted parameters in the multiple regression model.

Fluxes were estimated with the regression-model method using Load Estimator (LOADEST), a FORTRAN-based flux estimation program (Runkel and others, 2004). LOADEST requires a minimum of 12 samples, 7 of which must be uncensored, in order to calibrate a regression model and estimate fluxes. LOADEST allows users to choose from three methods to estimate fluxes on the basis of the statistical distribution of the calibration dataset. The method selected to estimate fluxes for this study was the adjusted maximum likelihood estimate (AMLE), which is appropriate for estimation when a dataset contains censored data. The AMLE method corrects for first-order bias in the regression coefficients (because of the presence of censored data in the calibration dataset) and minimizes other biases, such as when estimated logarithms of flux are retransformed to original units (Cohn and others, 1992). LOADEST gives users the option to automatically select an optimal model form from nine combinations of parameters based on equation 2 (model forms include eq. 2 and eight predefined subsets of the parameters in eq. 2). Auto-selection involves computation of the Akaike Information Criterion (AIC) statistic, as described in Judge and others (1988), and the model form with the lowest AIC value was selected.

Although AMLE fluxes are estimated by LOADEST on a daily time step, fluxes are reported here on a monthly time step because of potentially large errors in estimating fluxes for short time intervals. Even at a monthly time step, fluxes can be imprecise; to account for such uncertainty, LOADEST provides lower and upper 95-percent confidence intervals for each flux estimate so that the differences between flux estimates can be assessed appropriately. The confidence intervals are based on the standard error of prediction, which includes both the estimated parameter uncertainty and the unexplained variability associated with the model, referred to as random error (Runkel and others, 2004). When describing the uncertainty and errors associated with using a regression-based program, such as LOADEST, an assumption is made that there is negligible error in the daily streamflow measurements. Furthermore, error estimates assume that errors in the model are distributed randomly in time (no serial correlation), which can often be untrue and could be particularly unlikely during the 2011 flood. Failure to meet these two assumptions results in underestimated uncertainty.

The regression-model method is the preferred approach to estimate fluxes when there are a sufficient number of samples and there are significant concentration relations to develop a reasonably strong concentration-regression model, but sampling is insufficiently frequent to get accurate flux estimates using a period-weighted approach. Regression-model flux estimates presented therein are calculated using the same approach as Aulenbach and others (2007).

The third approach used to estimate fluxes in this study is the composite method (Aulenbach and Hooper, 2006), a hybrid flux estimation method that combines aspects of the period-weighted and regression-model approaches described previously. The composite method uses the regression-model method to predict variations in concentrations between collected samples and uses a period-weighted approach to apply the residual concentrations from the regression model over time. Residual concentrations are the difference between the observed and model-predicted concentrations. In this approach, on days with observations, the model-predicted concentrations are adjusted to observed concentrations; on days between observations, the model-predicted concentrations are adjusted by applying a piecewise linear function of the residual concentrations using a period-weighted approach. This approach is useful for situations in which there is serial autocorrelation in the residuals (that is, residuals are not independent and identically distributed), such that there is structure (or pattern) in the residuals that contain some meaningful information that can be used to improve flux estimates. When sampling frequency is increased, serial autocorrelation between samples generally increases, and the composite method should improve the estimates when the predicted regression-model concentrations are adjusted to match observed concentrations, thereby improving model fit.

The composite-method was preferred for flux estimation on the 2011 flood. For many constituents and stations, the sampling frequency was either weekly or biweekly from April through July so the composite method provided improved estimates by adjusting the AMLE-predicted concentrations to observed data. Although, there is no way to estimate the uncertainty associated with the composite method, flux estimates based on samples at 15-day intervals should be at least as accurate as fluxes estimated using the LOADEST AMLE method alone. The composite-method fluxes presented here use the same regression models developed to estimate LOADEST AMLE fluxes. Composite-method flux estimates have previously been reported in Aulenbach and others (2007), but only for water-quality station numbers 6 and 9. Unpublished results of a subsampling analysis using a daily suspended-sediment dataset indicated that when sampling frequencies are 15 days or less, the composite method can improve the precision of annual to monthly flux estimates, as compared to the AMLE approach. This subsampling analysis also indicated, however, that flux estimates were more precise with the AMLE approach for sampling frequencies of at least once per month. Another consideration for using the composite method is that regression models may be poorly constrained at the highest streamflows during a flood because (1) some constituents exhibit hysteresis in which the concentrations on the rising limb of the flood hydrograph do not match those on the falling limb of the hydrograph (regression model will predict average response at a particular streamflow) and (2) there are only a few water-quality observations at the highest streamflows.

Flux Estimation Implementation

Fluxes were estimated for the 2011 flood and are summarized therein on a monthly basis. Fluxes were estimated for nine constituents: dissolved nitrate plus nitrite, total organic nitrogen plus ammonia (total Kjeldahl nitrogen), total phosphorous, dissolved orthophosphate, suspended sediment (including suspended sand), simazine, atrazine, metolachlor, and acetochlor. In addition to these constituents, total nitrogen fluxes were estimated by summing dissolved nitrite plus nitrate and total Kjeldahl nitrogen fluxes. Suspended sediment flux was also estimated for the Red River at Alexandria, La.

Except for station number 5, regression models were calibrated at each water-quality station using the samples collected during a 5-year period, water years 2007 through 2011. A water year is the period from October 1 to September 30 and is identified by the year in which the period ends. The calibration period was set such that it was long enough to contain enough sample concentrations to sufficiently develop the regression model while not being so long that there are substantial changes, or drift, in the model regression over the calibration period. The calibration period used to develop the regression model corresponds to the calibration period that will be used for estimating fluxes at all NASQAN stations for the 2011 water year. At water-quality station number 5, only a 3-year period was used for calibration, 2009 through 2011, because water-quality sampling at this station was only recently initiated.

The fluxes for water-quality station number 6, downstream from the Old River Control Structure (where, on average, about 25 percent of the Mississippi River streamflow is diverted to the Atchafalaya River) were estimated using a complex regression model used by the USGS to estimate fluxes at NASQAN stations (Aulenbach and others, 2007). Rather than only using streamflow for the Mississippi River at Tarbert Landing, Miss., to develop the regression model, this streamflow was combined with streamflow diverted through the Old River Control Structure. The combined streamflow more accurately reflects the variations in streamflow associated with changes in constituent concentrations near station number 6. Furthermore, it was found that variations in water quality at station number 6 were related to variations in streamflow contributions from the upper Mississippi and the Ohio River Basins. Therefore, streamflow and streamflow-squared terms for the upper Mississippi River and the Ohio River were added to the regression models. These streamflows were lagged by 10 days to account for average travel times for streamwater from these upstream stations to reach water-quality station number 6 during average streamflow conditions. The use of this customized model form with additional variables precluded the use of the LOADEST feature of auto-selecting the best model by using the lowest value of the AIC statistic; hence, all model terms were always included. For flux estimates to represent only the proportion of streamflow at water-quality station number 6, daily flux estimates from the model were multiplied by the ratio of Mississippi River streamflow at Tarbert Landing, Miss., to streamflow of the entire lower Mississippi River subbasin.

Fluxes were not directly estimated at the Old River Control Structure, Bonnet Carré Spillway, and Morganza Floodway because there were insufficient long-term water-quality data at these stations. Instead, water quality at station number 6 and streamflow at Tarbert Landing were used with the regression-model and composite methods to estimate fluxes. For each location, estimated fluxes were prorated based on the ratio of streamflow at the Old River Control Structure, Bonnet Carré Spillway, or Morganza Floodway to streamflow at Tarbert Landing. Water quality at the control structures is likely to be similar to the water quality measured in samples from station number 6 because of the proximity of the control structures to the station. The flux estimates for the control structures are probably reasonable for dissolved constituents because these constituents are likely to be well mixed in the water column. Suspended sediment, particulate, and total constituent fluxes may be overestimated because some suspended material may settle out of the water column before entering these control structures. The flux estimates based on water quality at station number 6 and streamflow at Tarbert Landing represent the fluxes at Tarbert Landing (not at station number 6), because streamflow and fluxes have not been adjusted for streamflow diverted into the Morganza Floodway during the 2011 flood, which is downstream of Tarbert Landing but upstream of station number 6.

In May 2011, flux estimates for water-quality station number 4 were complicated by backwater conditions that occurred during the flood that month. Streamflow in the Yazoo River was not elevated because the Yazoo River was not flooded during this time. Backwater conditions, in which floodwater from the Mississippi River flowed upstream into the lower Yazoo River, resulted in 20 days of negative daily average streamflow in May at water-quality station number 4. For these days, it was assumed the stream water quality was similar to that of water-quality station number 5. Therefore, the flux on these days was calculated as the daily flux from water-quality station number 5, prorated by the ratio of Yazoo River streamflow to Mississippi River streamflow above Vicksburg. The streamflow station for the Mississippi River is at Vicksburg, Miss., downstream from the confluence of the Yazoo River; hence, the streamflow for the Mississippi River above Vicksburg is calculated as the difference between Mississippi River streamflow at Vicksburg and Yazoo River streamflow. The average streamflow and all of the fluxes along the Yazoo River were negative in May 2011, indicating net streamflow and fluxes in the upstream direction because of Mississippi River backflooding into the lower Yazoo River.

Sampling of suspended-sediment in the Bonnet Carré Spillway and Morganza Floodway during the 2011 flood was sufficient to estimate suspended-sediment fluxes using the period-weighted approach. These fluxes are probably more representative than those obtained using the regression-model and composite-method estimates, which assume that the diversions have the same suspended-sediment concentrations as those measured in samples collected at water-quality station number 6.

Fluxes for streamflow, total nitrogen, nitrite plus nitrate, orthophosphate, total phosphorus, atrazine, metolachlor, acetochlor, simazine, suspended sand, and suspended sediment for the 2011 flood are discussed at select individual water-quality stations, and inputs from the upper Mississippi River and the Ohio River are compared to outputs to the Gulf of Mexico. Output to the Gulf of Mexico was calculated by adding fluxes from water-quality station numbers 6, 9, and 11 and then subtracting fluxes from the Morganza Floodway and Bonnet Carré Spillway (water-quality station numbers 12 and 13). One issue with this approach is the travel time between the stations, because stations near one another do not exhibit the same time lag in constituent travel as those located farther apart. In addition, fluxes to the Gulf of Mexico from the lower Mississippi River were based on estimates at water-quality station number 6, which is about 265.5 river mi above the mouth of the Mississippi River.

Statistical Methods

An analysis of variance was used to test if the means of atrazine, acetochlor, metolachlor, and simazine concentrations from April through July of 2011 differed between sampling stations. If the null hypothesis was rejected (indicating the means differed) then Tukey's multiple comparison test (Helsel and Hirsch, 1992, p. 196) was used to determine which sampling stations had different means. Additionally, the analysis of variance was used to test whether the historical mean concentrations for April through July were different than the mean concentrations during the 2011 flood. The tests were considered significant at the 5-percent level. The analysis of variance is a parametric test and assumes a normal distribution and equal variances, which is not always true with water-quality data. For non-normal data, a nonparametric test can be more powerful in detecting when the null hypothesis is false. Using ranked data with parametric tests is more appropriate in the case of non-normal data; therefore, the procedures just described were conducted using rank-transformed data and any differences were noted.

Suspended Sediment Concentrations and Transport

Suspended-sediment concentrations measured in surface water at nine stations in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood were within the range of concentrations measured historically at these stations (fig. 3). Median suspended-sediment concentrations for samples collected during the 2011 flood at water-quality stations 1 and 2 were higher than historical medians at these stations (fig. 3). Median suspended-sediment concentrations measured during the flood at stations located downstream of the confluence of the upper Mississippi and Ohio Rivers (station numbers 5 through 11) were lower than the historical medians at each of these stations (fig. 3).

High concentrations of suspended sediment were measured in water at water-quality stations 1, 5, and 6 in early March 2011 (fig. 4). Samples collected downstream from these three stations, as well as samples from the three stations on the Atchafalaya River, also had high suspended-sediment concentrations in March (data not shown). The concentration of suspended sediment on March 8, 2011, at station 1 (529 mg/L) was about 1.2 times higher than the maximum suspended-sediment concentration measured during the 2011 flood (448 mg/L on June 7, table 1). The concentration of suspended sediment on March 1 at station 5 (610 mg/L) was about four times higher than the maximum suspended-sediment concentration of 164 mg/L measured during the 2011 flood on May 13, 2011 (table 1). The suspended-sediment concentration measured on March 8 at station 6 (569 mg/L) was about three times higher than the maximum concentration of 179 mg/L measured on July 11, 2011 (table 1). At most of the stations, concentrations of suspended sediment were low during times of maximum streamflow (fig. 4). As streamflow decreased, suspended-sediment concentrations typically increased. The low suspended-sediment concentrations measured during the 2011 flood at stations in the lower Mississippi-Atchafalaya River subbasin (fig. 4) were most likely a consequence of the storm event in early March, which occurred when most agricultural fields in the subbasin were being prepared for the growing season. This preparation created optimal conditions for suspended-sediment removal by overland runoff, thereby diminishing the supply of suspended sediment available for transport when the flooding occurred (fig. 4). Another contributor to low suspended-sediment concentrations at the time of maximum streamflow was the Ohio River, which composed the greater fraction of streamflow during April and May than the upper Mississippi River. Suspended-sediment concentrations in the Ohio River were lower than concentrations in the upper Mississippi River, resulting in a dilution effect. As stage along the Mississippi River fell, the upper Mississippi River contributed relatively more water to the lower Mississippi-Atchafalaya River subbasin and floodwater carrying sediment from inundated lands and tributaries in backwater flowed into the lower Mississippi

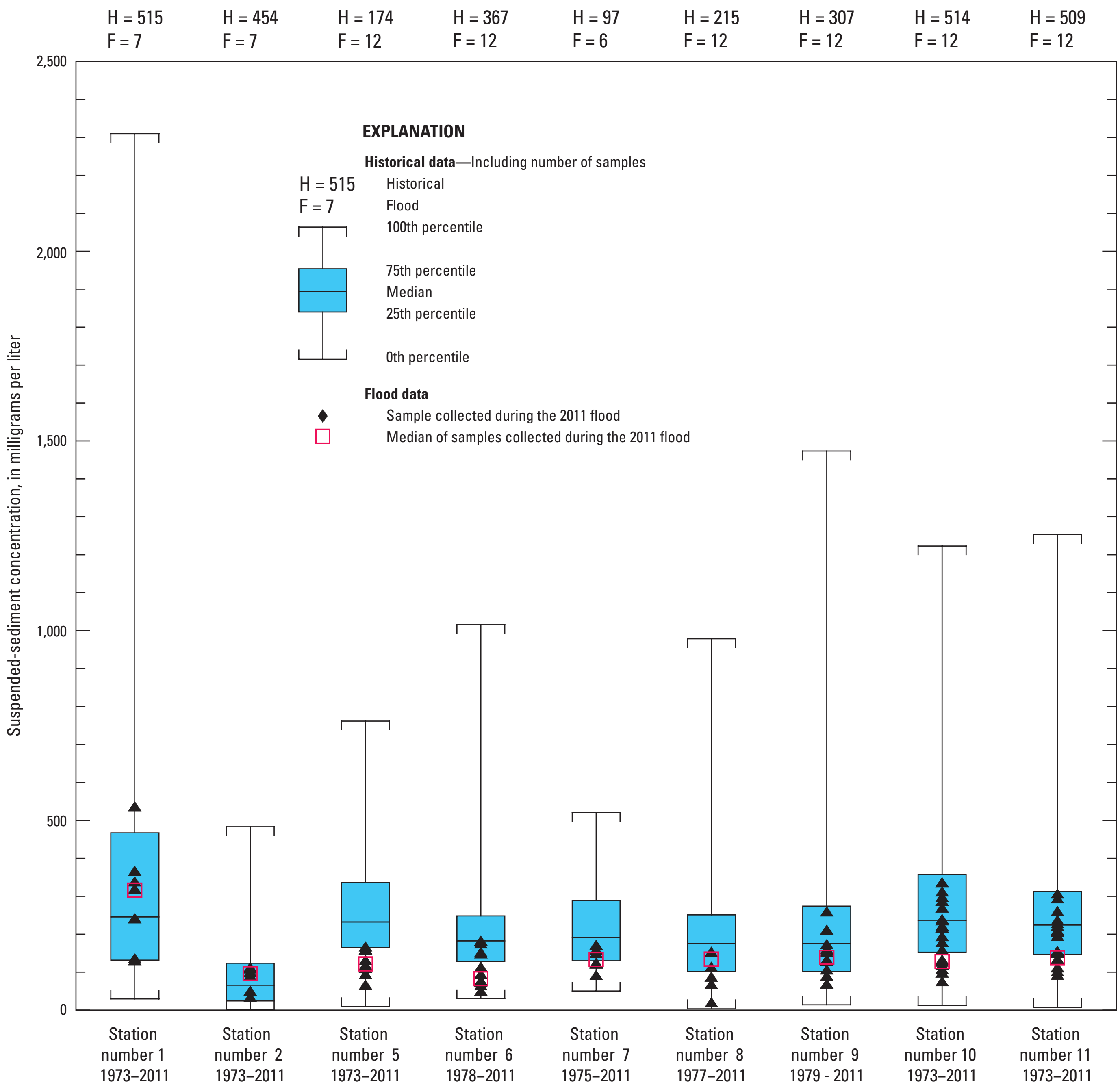

Figure 3. Concentrations of suspended sediment measured during the 2011 flood compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record.

River, thus explaining the increase in suspended-sediment concentrations at stations 5 and 6 following the peak streamflow (fig. 4).

Although suspended-sediment concentrations measured during the 2011 flood were similar to historical concentrations in the lower Mississippi-Atchafalaya River subbasin, fluxes during the 2011 flood were quite high because of high streamflow. The majority of the suspended-sediment flux into the subbasin during the flood entered through the upper Mississippi River, despite the fact that the contribution of streamflow to the subbasin during the 2011 flood period was approximately equal between the upper Mississippi and Ohio Rivers and that reservoirs constructed along the Missouri and Arkansas Rivers had cut off the largest natural source of sediment to the Mississippi River (fig. 5 and table 2; Meade, 1995). The annual suspended-sediment flux from water-quality station number 1 in 2011 (126 million metric tons) was in the middle-range of historical fluxes (table 2); the flux

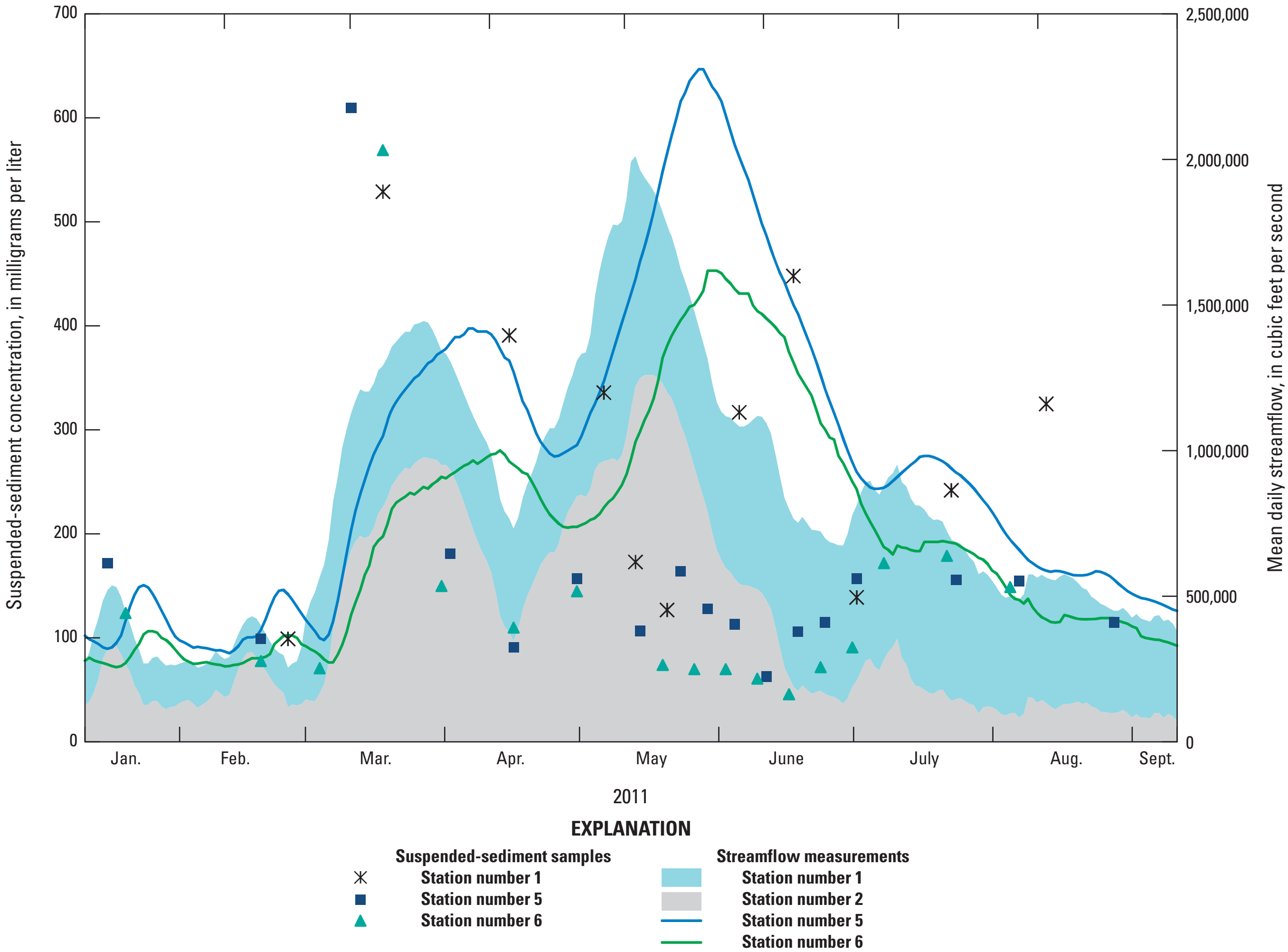

Figure 4. Suspended-sediment concentration and streamflow from water-quality station numbers 1, 2, 5, and 6 for January through August 2011. Streamflow from station number 1 was added to streamflow from station number 2 to obtain a cumulative streamflow represented by the entire shaded area.

of 47.7 million metric tons for the 2011 flood was 38 percent of the 2011 annual flux. Suspended-sediment flux at water-quality station number 2 in 2011 (35 million metric tons) was near the lower end of the range of historical fluxes (table 2). The suspended-sediment flux of 11.9 million metric tons from the Ohio River for the 2011 flood was 34 percent of the 2011 annual flux (table 2).

The contribution of station number 1 to the suspended-sediment flux moving into the lower Mississippi-Atchafalaya River subbasin during the 2011 flood was about 77 percent of the total suspended-sediment flux, and flux from the upper Mississippi River was four times the flux from the Ohio River (fig. 5; table 2). This is similar to the 75-percent annual-average contribution to suspended-sediment flux by the Missouri River (which lies within the upper Mississippi River subbasin) estimated by Pereira and Rostad (1990). Another 2.66 million metric tons of suspended sediment was introduced to the lower Mississippi River from station number 3. From the confluence of the upper Mississippi and Ohio Rivers to water-quality station number 5, there was a 17-percent loss in suspended-sediment flux totaling 10.3 million metric tons for the 2011 flood. The Yazoo River was in backwater in May 2011, which caused a 171,000-metric-ton loss of suspended-sediment flux in the lower Mississippi River above water-quality station number 5. Despite the loss, estimated suspended-sediment flux at this station totaled 49.3 million metric tons, which was larger than the flux at any other water-quality station during the 2011 flood (table 2; fig. 5). The annual suspended-sediment flux of 105 million metric tons in 2011 at water-quality station number 5 was near the middle-range of historical fluxes (table 2); 47 percent of the 2011 annual flux at this station was from the 2011 flood.

During the 2011 flood, 11.53 million metric tons of suspended sediment (23 percent of the flux at Vicksburg, Miss.) was diverted through the Old River Control Structure into the Atchafalaya River (fig. 5). Horowitz (2010) noted

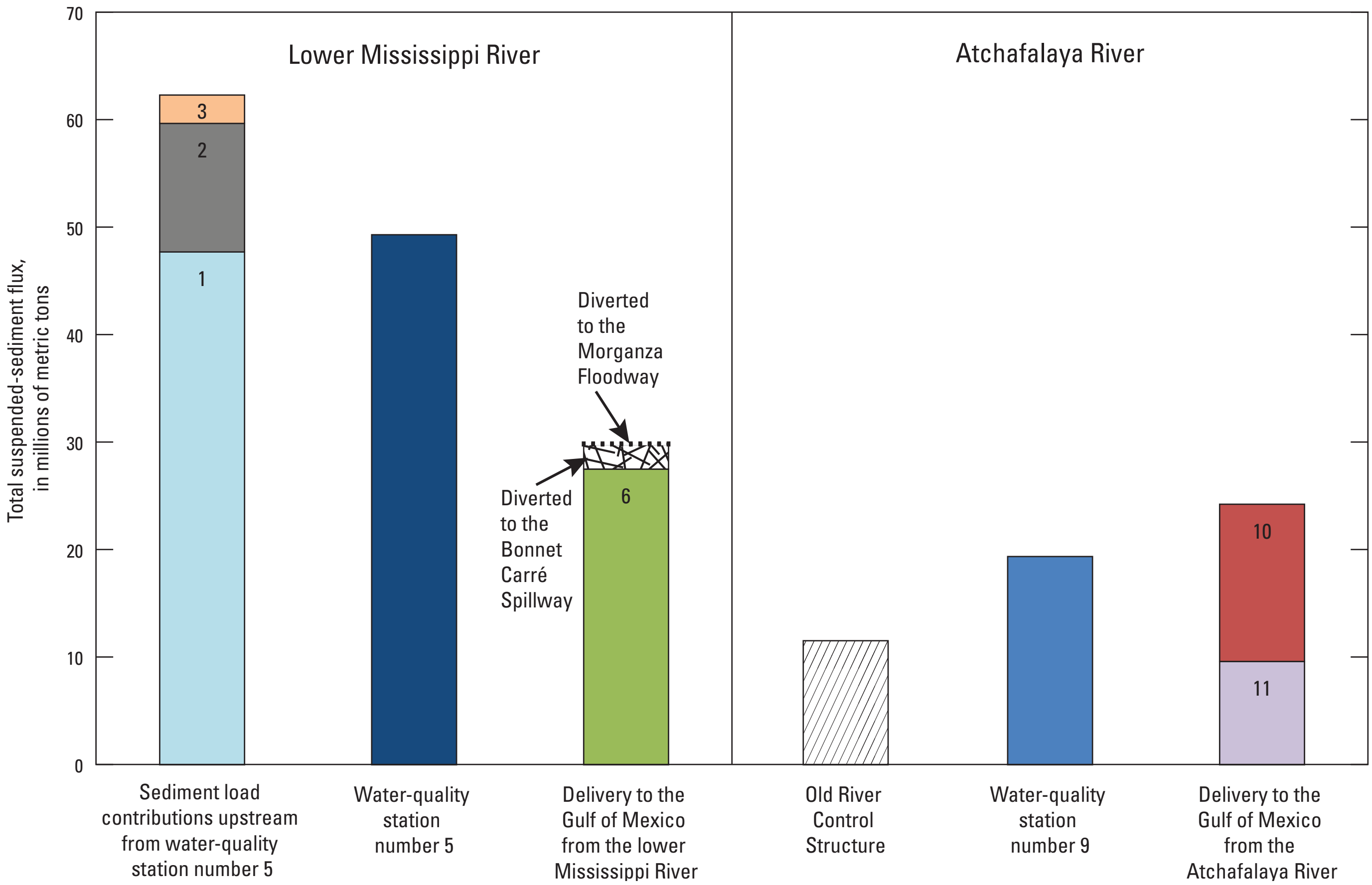

Figure 5. Cumulative suspended-sediment flux in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July. Pattern fills denote a diversion of suspended-sediment flux. Numbers within the bars correspond to the water-quality station numbers in table 1.

that from 1981 through 2007, the annual suspended-sediment flux diverted through the Old River Control Structure ranged from 14 to 52 million metric tons. The 2011 annual flux at the Old River Control Structure was 24 million metric tons, 49 percent of which is attributed to the 2011 flood. An additional 9.7 million metric tons of suspended-sediment flux (21 percent) was lost between the Old River Control Structure and water-quality station number 6. The flood-period suspended-sediment flux at water-quality station number 6 (29.9 million metric tons; fig. 5; table 2) was 49 percent of the 2011 annual flux of 61.3 million metric tons, which was near the lower end of the range in annual suspended-sediment flux measured from 1981 through 2007 (table 2). Eight percent of the suspended-sediment flux at water-quality station number 6 was diverted into the Morganza Floodway and Bonnet Carré Spillway during the 2011 flood (May and June only; fig. 5; table 2).

Suspended-sediment flux increased as flood-water moved through the Old River Control Structure into the Atchafalaya River and downstream to the Gulf of Mexico. A 68-percent gain in suspended-sediment flux (7.82 million metric tons) occurred before the water reached water-quality station number 9 (fig. 5; table 2). A depositional area is located at the bend in the Atchafalaya River near its confluence with the Red River (fig. 2; Barb Kleiss, U.S. Army Corps of Engineers, oral commun., 2011), and high streamflow in May most likely resuspended this sediment and deposited it downstream. Although the Red River could have contributed all of the gain in suspended-sediment flux before water-quality station number 9, the average streamflow in the Red River during the 2011 flood was 16,900 ft^3/s, which most likely was insufficient for the transport of 7.82 million metric tons of suspended sediment. Between water-quality station number 9 and station numbers 10 and 11, suspended-sediment flux increased further (25 percent, 4.86 million metric tons) (fig. 5; table 2). The increase in flux between the stations could be explained by the resuspension of sediment by high streamflows. The suspended-sediment flux for the 2011 flood at station numbers 10 and 11 composed 55 percent of the 2011 suspended-sediment flux (43.7 million metric tons) that entered the Gulf of Mexico through the Atchafalaya River.

Table 2. Flux of suspended sediment and suspended sand in the lower Mississippi-Atchafalaya River subbasin, April–July 2011.

[All fluxes in metric tons, except for suspended-sediment flux and suspended-sand flux which are in 10^6 metric tons. USGS, U.S. Geological Survey; --, not estimated]

Water-quality station number	USGS station name	Suspended-sediment flux			Suspended-sand flux, 2011 flood
		2011 flood	2011 annual	Historical annual	
Lower Mississippi River stations					
1	Upper Mississippi River	47.7	126	25–200[b]	7
2	Ohio River	11.9	35	15–90[b]	1.1
5	Vicksburg	49.3	105	30–180[b]	14.5
6	Saint Francisville	29.9	61.3	30–165[b]	8.3
	Saint Francisville minus the two flood-control structures[a]	27.5	--	--	8.2
Atchafalaya River stations					
9	Melville	19.4	30.9	12.2–96.7[c]	7.6
10	Morgan City	14.6	24.8	10.3–70.7[d]	6.0
11	Wax Lake	9.6	18.9	6.1–45.2[d]	1.9
Total flux delivered to the Gulf of Mexico		51.7	105	48–321[e]	16.1

[a]The two flood-control structures are the Bonnet Carré Spillway and the Morganza Floodway.

[b]For the time period 1981–2007 (Horowitz, 2010).

[c]For the time period 1984–1993 and 1996–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[d]For the time period 1973–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[e]For the time period 1978–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

The annual 2011 suspended-sediment (105 million metric tons) to the Gulf of Mexico was near the lower end of the range of historical fluxes (table 2). Approximately half (51.7 million metric tons) of the annual 2011 suspended-sediment flux was delivered to the Gulf of Mexico during the 2011 flood. When comparing the suspended-sediment flux inputs with the suspended-sediment flux outputs in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, 7.9 million fewer metric tons of sediment (13 percent) left the subbasin than entered it from the confluence of the upper Mississippi and Ohio Rivers (table 2). Figure 5 shows a steady decline in suspended-sediment flux with downstream distance along the lower Mississippi River. In contrast, there is an increase in suspended-sediment flux between the Old River Control Structure and subsequent stations downriver along the Atchafalaya River. Most of the 13-percent loss in flux probably occurred along reaches of the lower Mississippi River in depositional areas between the Arkansas River and Vicksburg and also between the Old River Control Structure and St. Francisville. The loss in suspended-sediment flux is probably related to a reduction in stream power below the Old River Control Structure, which has resulted in an area of channel aggradation between Tarbert Landing and St. Francisville (Allison and others, 2012). In addition, losses in suspended-sediment flux probably occur below water-quality station number 6 as noted by Allison and others (2012), who state that from 2008 through 2010, only 19 percent of the suspended-sediment flux at Tarbert Landing (above St. Francisville) reached the deepwater Gulf of Mexico through the lower Mississippi River. Opening the Bonnet Carré Spillway also reduced the stream power in the lower Mississippi River, which resulted in sand deposition immediately downriver of the spillway (Allison and others, 2013). Although there were gains in flux in the Atchafalaya River Basin during the 2011 flood, 12 percent more suspended sediment was delivered to the Gulf of Mexico from the lower Mississippi River than from the Atchafalaya River (27.5 and 24.2 million metric tons, respectively, (table 2) probably because more streamflow passed through the lower Mississippi River.

Transport of Suspended Sand During the 2011 Flood

Low sand-fraction percentages (median values $\leq$13 percent) at water-quality station numbers 1 and 2 indicate a lack of available material for resuspension, even during high streamflow (table 1). In most streams, high streamflow is typically an effective transport mechanism for sand-sized particles (Allison and others, 2012). Even during peak streamflows, however, the sand-fraction percentage at station number 1 was below 10 percent. At this station, there was a slight negative correlation between streamflow and sand-fraction percentage (ρ-value <0.05; fig. 6*A*) during the 2011 flood. Long-term sand-fraction percentage data from station number 1 (1977–2011; data not shown) indicated a negative correlation between streamflow and the sand-fraction percentage (ρ-value <0.05). Holmes (1996) found no definite trend in coarsening or fining of suspended sediment with streamflow at station number 1 in samples collected prior to and during the 1993 Mississippi River flood. There was a strong positive correlation between streamflow and sand-fraction percentage at station number 2 (ρ-value <0.05; fig. 6*A*) during the 2011 flood. Although there was an increase in sand-fraction percentage with streamflow at station number 2, the percentage never exceeded 20 percent, even for streamflows in excess of 1 million ft^3/s (fig. 6*A*).

Allison and others (2012) noted that the lower Mississippi River and Atchafalaya River distributary pathways are efficient at removing sediments from suspension, particularly sand. These deposited sediments most likely were resuspended and transported with the high streamflows during the 2011 flood. There were positive correlations between streamflow and sand-fraction percentage at station numbers 5 through 7 on the lower Mississippi River and station numbers 9 through 11 on the Atchafalaya River (ρ-value <0.05; fig. 6*B*). During the 2011 flood, sand-fraction percentages at the three lower Mississippi River stations were not below 10 percent in samples collected during minimum streamflows (table 1). Maximum sand-fraction percentages (about 60 percent) were higher at station numbers 5 and 7 compared to percentages at other sites on the lower Mississippi and Atchafalaya Rivers (table 1; fig. 6*B*). As previously stated, diverting streamflow through the Old River Control Structure between station numbers 5 and 6 probably resulted in a loss of stream power that decreased the carrying capacity of suspended sediment along this portion of the stream reach. Fine- and coarse-grained materials in the area of aggradation between station numbers 6 and 7 were probably resuspended during high streamflow, resulting in a higher percentage of coarse-grained sediment farther downstream. The sand-fraction percentage was highest in the Atchafalaya River at station number 9, which is most likely related to the resuspension of sediment in the depositional area located at the bend in the Atchafalaya River and its confluence with the Red River (table 1; fig. 6*C*). The presence of higher sand-fraction percentages in water from stations along the lower Mississippi River and the Atchafalaya River as compared to station numbers 1 and 2 indicate that the upper Mississippi and Ohio Rivers were

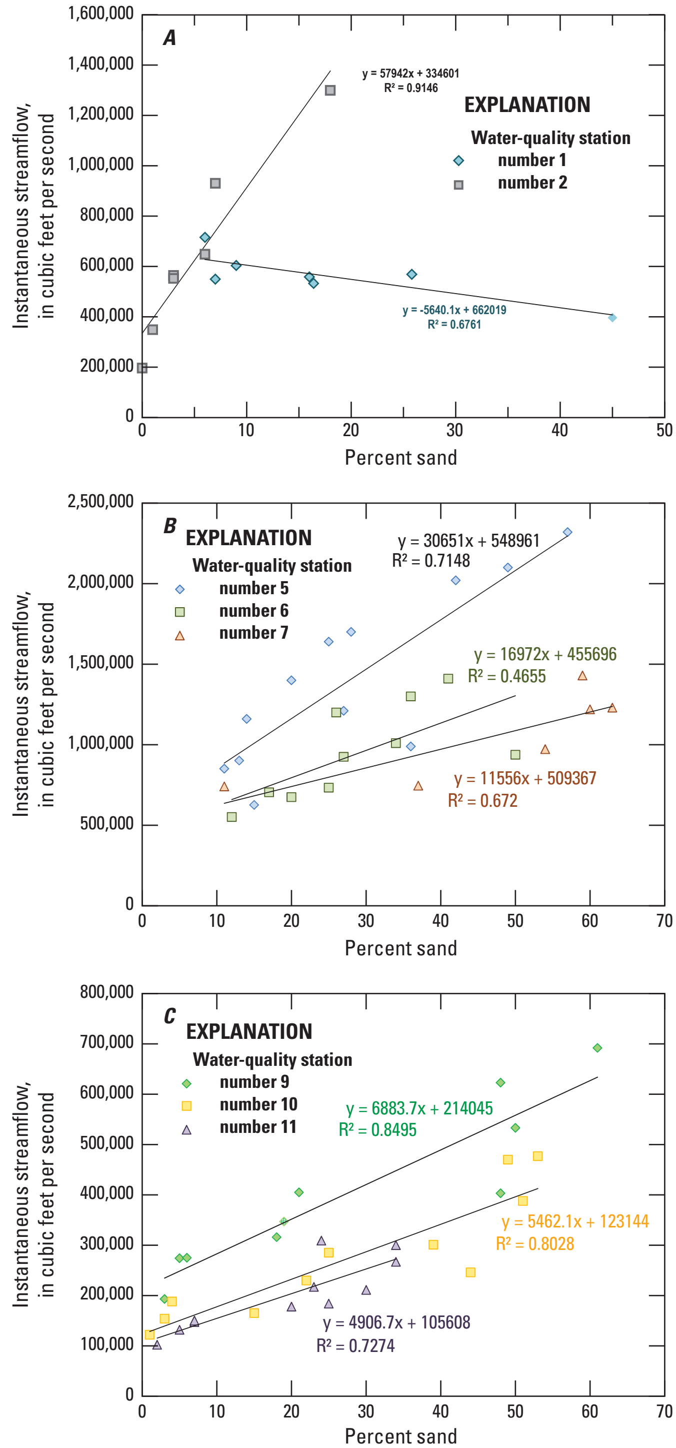

Figure 6. Relation between streamflow and sand-fraction percentage at *A*, stations above the confluence of the upper Mississippi and Ohio Rivers, *B*, stations on the lower Mississippi River, *C*, and stations on the Atchafalaya River, April–July 2011.

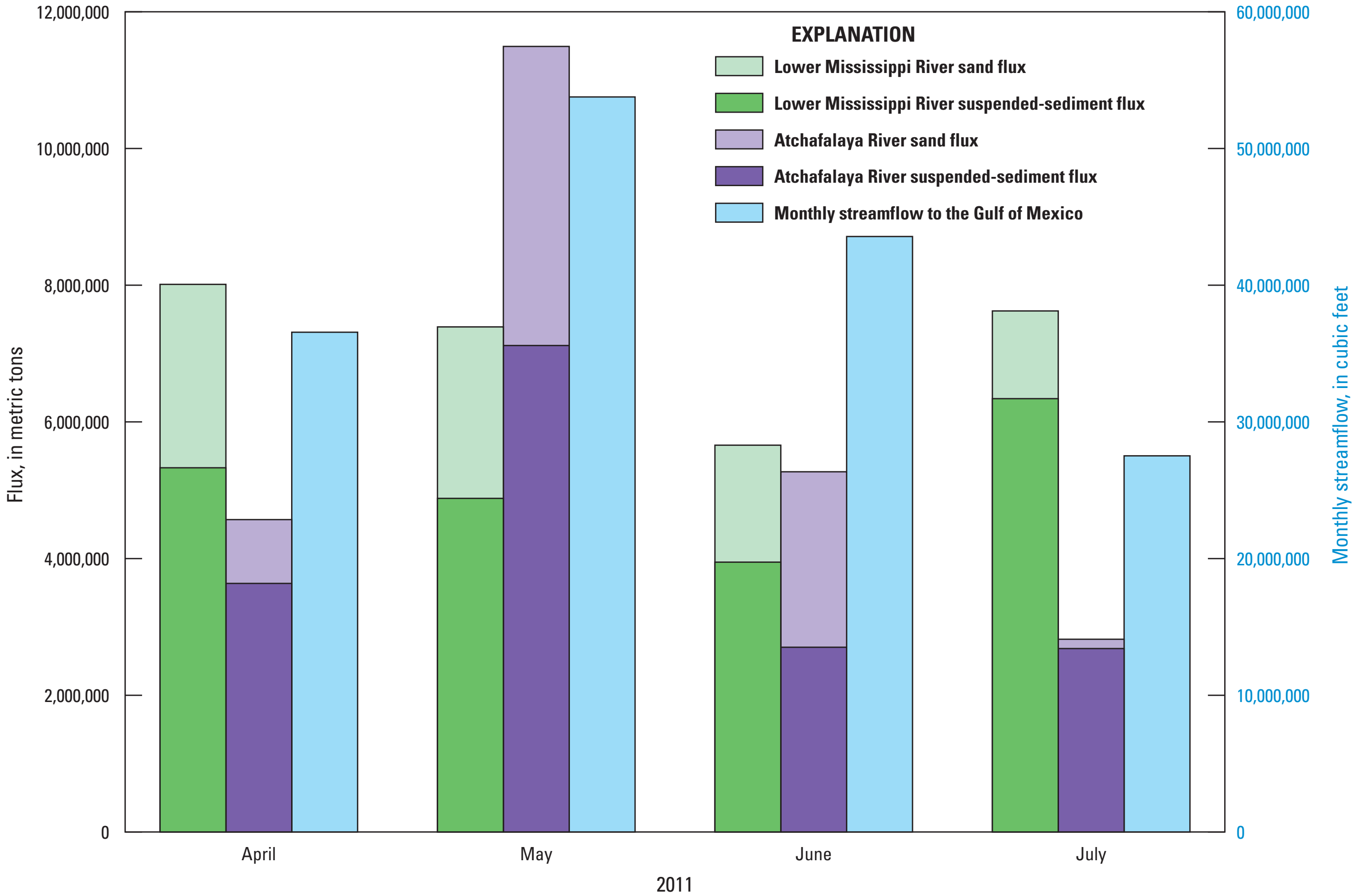

Figure 7. Monthly suspended-sediment and suspended-sand flux delivered to the Gulf of Mexico from the lower Mississippi River and the Atchafalaya River. The bar showing sand flux represents its portion of the suspended-sediment flux; thus, total suspended-sediment flux is the sum of the two bars together.

not the source of the sand-size particles in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood.

According to Roberts (1998), the Atchafalaya/Wax Lake delta is the only location in the lower Mississippi-Atchafalaya River subbasin where sufficient sediment is available for delta-building to occur. In contrast, the Bird's Foot delta of the Mississippi River has been documented to be eroding (Roberts, 1998) since the late 1990s. During the 2011 flood, the suspended-sand flux that entered the Gulf of Mexico from the lower Mississippi River and through the Atchafalaya River was comparable (8.2 million and 7.9 million metric tons, respectively; table 2). Similar to suspended-sediment flux, however, gains in suspended-sand flux occurred between all stations along the Atchafalaya River, whereas in the lower Mississippi River, there were losses in suspended-sand flux between all stations downstream from station number 5 (table 2). The largest gain (+138 percent) in suspended-sand flux during the 2011 flood occurred in the reach between the Old River Control Structure and station number 9. When comparing the suspended-sand flux inputs with the suspended-sand flux outputs in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, approximately 99 percent (8 million metric tons) more sand left the subbasin than entered it from the confluence of the upper Mississippi and Ohio Rivers (table 2).

Monthly fluxes of suspended sediment and suspended sand seemed more responsive to increases in streamflow at water-quality stations on the Atchafalaya River than did fluxes at stations on the lower Mississippi River (fig. 7). At the lower Mississippi River stations, the highest streamflows were measured in May (Welch and Barnes, 2013), yet sediment fluxes were less in May than in April and July. In contrast, fluxes on the Atchafalaya River increased with increasing streamflow in May and then decreased throughout the remainder of the 2011 flood (fig. 7). The largest monthly flux of suspended sand was delivered from the Atchafalaya River in May (4.4 million metric tons). Based on these data, it appears that sequestered sand-sized material in the Atchafalaya River was more readily available for transport during high streamflow events than sand-sized material on the lower Mississippi River.

The modeled estimate of sand flux at station number 13 during the 2011 flood was 165,150 metric tons (about 2 percent of the lower Mississippi River sand flux). Water-quality station number 13 is located approximately 2.5 mi into the

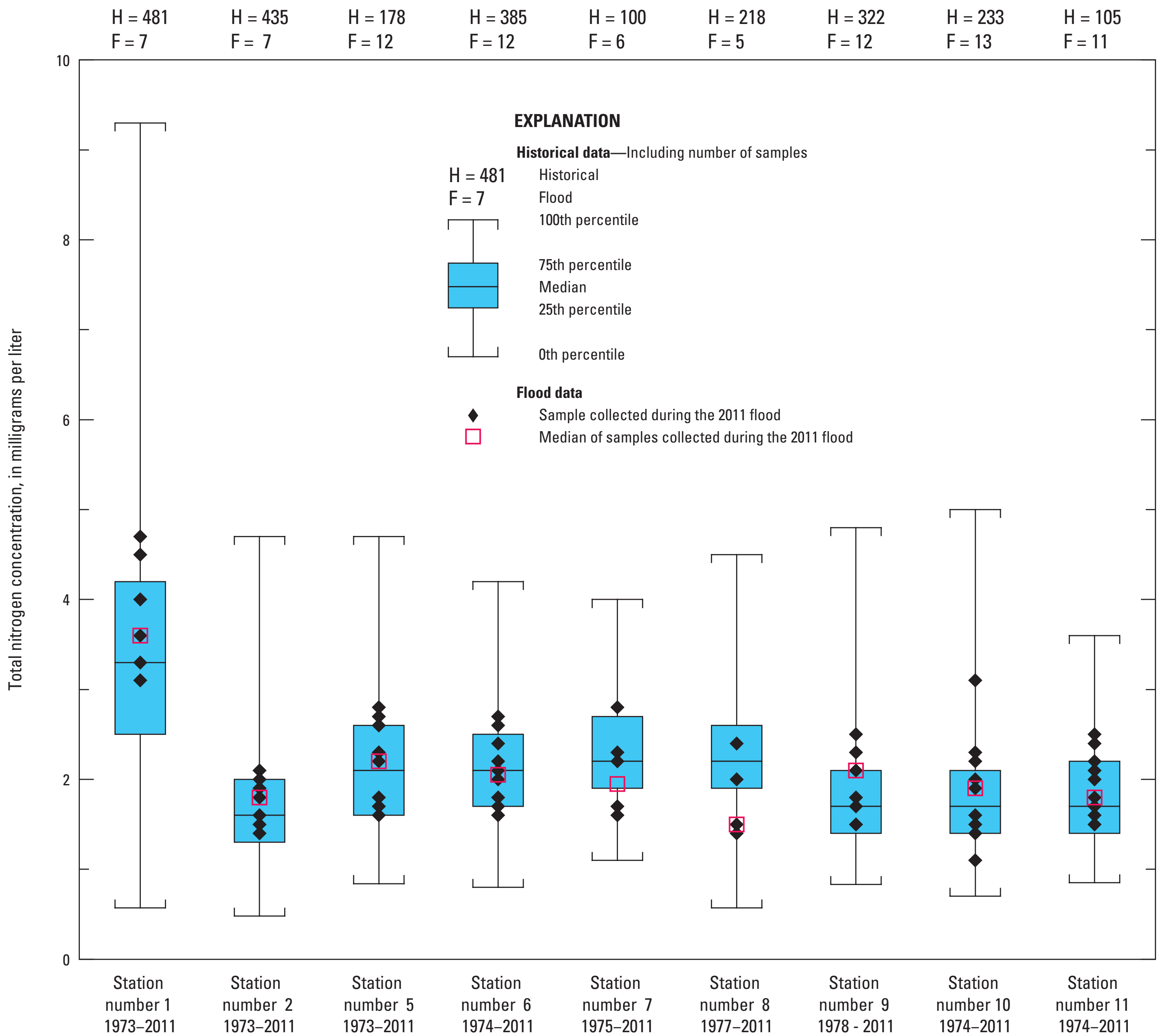

Figure 8. Concentrations of total nitrogen during the 2011 flood compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record.

Bonnet Carré Spillway, so there was no direct measurement of the suspended-sediment or sand flux that entered through the spillway gates. Nittrouer and others (2012) estimated that 31 to 46 percent of the lower Mississippi River sand flux was diverted through the Bonnet Carré Spillway while it was in operation, but the flux was deposited within 1.5 mi of the spillway opening. A percentage of Nittrouer's estimate of sand flux during the 2011 flood might be from sand stored prior to the flood, rather than directly contributed from the channel-suspended plus bedload flux (Allison and others, 2013). Allison and Meselhe (2010) used data from the 1997 opening of the spillway to show that much of the sand that passed through the structure was deposited within 0.6 mi downstream of the structure opening and upstream of station number 13.

Nutrient Concentrations and Transport

Median total nitrogen concentrations measured in water during the 2011 flood were higher than the historical median concentrations at station numbers 1, 2, 5, and 9 through 11 (fig. 8). Conversely, median total nitrogen concentrations during the 2011 flood were lower than historical medians at stations on the lower Mississippi River downstream of the Old River Control Structure (station numbers 6 through 8). Higher total nitrogen concentrations during the 2011 flood compared to historical data at station numbers 1 and 2 might be attributed to the flood coinciding with application periods of agricultural fertilizer in the upper Mississippi River subbasin (particularly lands drained by the Missouri River) and to a lesser extent, the Ohio River subbasin. Total nitrogen concentrations measured at station number 1 were higher than concentrations at any other sampled station during the 2011 flood (ranging from 3.1 to 4.7 mg/L, table 3). Total nitrogen concentrations at station number 5 ranged from 1.6 to 2.8 mg/L, falling between the respective concentration ranges measured at station numbers 1 and 2 and indicating the mixing of the two water sources that flow into the lower Mississippi-Atchafalaya River subbasin.

Nitrate has been linked to the formation of a zone of hypoxia in the Gulf of Mexico during late spring and early summer each year (Turner and others, 2008). High concentrations of nitrate were measured in water from station numbers 1, 5, 6, and 9 in early March, prior to the 2011 flood (fig. 9). Samples collected downstream from these stations on the lower Mississippi River and the Atchafalaya River also had high nitrate concentrations in March. Goolsby and others (1993b) and Goolsby and Battaglin (1997) observed that nitrate concentrations in streams are higher in the winter and spring compared to concentrations in the summer. The nitrate concentrations at station numbers 1 and 5 in March were less than the maximum nitrate concentrations measured during the 2011 flood at the two stations (fig. 9; table 3). However, the nitrate concentrations in early March at station numbers 6 and 9 were greater than the maximum nitrate concentrations measured during the 2011 flood at these two stations (fig. 9; table 3). During the 2011 flood, nitrate concentrations generally decreased as streamflow increased at station numbers 5, 6, and 9 (fig. 9). Although nitrate concentrations were highest at station number 1, they did not appear to be related to streamflow.

Nitrate concentrations decreased at station numbers 5, 6, and 9 during May to mid-June for a variety of reasons. During warmer months, nitrate is assimilated by terrestrial and aquatic plants, and there is also reduced leaching of nitrate from soils to streams (Goolsby and others, 1993b). In addition, the Ohio River was the primary source of streamflow contributing to the 2011 flood in the lower Mississippi-Atchafalaya River subbasin during May (Welch and others, 2012; Welch and Barnes, 2013). Clark and others (2002) showed that concentrations of most chemical constituents at the Old River Control Structure decreased as the percentage of water from the Ohio River increased. Because the Ohio River drains an area that is less intensively cultivated, has greater relief in elevation, and is more forested than lands drained by the upper Mississippi River (Clark and others, 2002), water from the Ohio River seemed to effectively dilute nitrate concentrations from May to mid-June. As streamflow decreased and the percentage of water contributed from the upper Mississippi River to the lower Mississippi-Atchafalaya River subbasin increased (Welch and others, 2012; Welch and Barnes, 2013), nitrate concentrations at station numbers 5, 6, and 9 increased (fig. 9).

The Mississippi River Basin has been identified as the dominant contributor of nitrogen to the zone of hypoxia in the Gulf of Mexico (Rabalais and others, 2002; Scavia and others, 2004; Alexander and others, 2008). More precisely, increased nitrate flux from the Mississippi River to the Gulf has resulted in eutrophication (or creation of large areas of algal blooms) that has altered the marine environment and has led to zones of anoxia or hypoxia along the inner continental shelf region off the coasts of Louisiana and Texas, and to a lesser extent, Mississippi. The majority of the total nitrogen and nitrate flux introduced into the subbasin during the 2011 flood was through the upper Mississippi River (table 4; fig. 10), which drains agricultural lands. During the 2011 flood, nitrate accounted for approximately 70 percent of the total nitrogen flux at all of the water-quality stations, except for the flux at station number 3 (nitrate flux composed about 50 percent of the total nitrogen flux). The annual nitrate flux from station number 1 in 2011 was 744,000 metric tons, which is within the range of historical fluxes (table 4), and the nitrate flux during the 2011 flood of 415,000 metric tons composed 56 percent of the 2011 annual flux (table 4). At station number 2, the 2011 annual nitrate flux was 309,000 metric tons, which is within the range of historical fluxes (table 4). The 2011 flood nitrate flux of 169,500 metric tons at station number 2 composed 55 percent of the 2011 annual flux (table 4).

The 2011 flood nitrate flux that entered the lower Mississippi River from the upper Mississippi River during the 2011 flood was 2.4 times greater than the nitrate flux that entered the lower Mississippi River from the Ohio River (fig. 10; table 4). The contribution of flux at station number 1 to the nitrate flux moving into the lower Mississippi-Atchafalaya River subbasin during the 2011 flood was about 71 percent, which is greater than the 50-percent average annual contribution documented by Meade (1995) and Goolsby and Battaglin (1997) and the 60-percent contribution documented by Goolsby and others (1993b) for April 1991 through March 1992. Another 8,670 metric tons of nitrate were delivered to the lower Mississippi River from the Arkansas River at water-quality station number 3. From the confluence of the upper Mississippi and Ohio Rivers to station number 5, there was a 0.9-percent gain in nitrate flux totaling 5,500 metric tons for the 2011 flood. In May 2011, the Yazoo River was in backwater, which accounted for a 1,050-metric-ton loss of nitrate flux in the lower Mississippi River above station number 5. Despite the loss, the estimated nitrate flux at Vicksburg (station number 5) was 590,000 metric tons, larger than the flux at any other water-quality station during the 2011 flood (table 4; fig. 10). Below station number 5, 163,600 metric tons of nitrate (28 percent of the flux at station number 5) was diverted through the Old River Control Structure into the Atchafalaya River (fig. 10). Despite the loss of flux that was diverted to the Atchafalaya River, there was a gain of 2,300 metric tons in nitrate flux between the

Table 3. Summary statistics for concentrations of selected nutrients from samples collected at surface-water stations in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July.

[All concentrations are in milligrams per liter (mg/L). USGS, U.S. Geological Survey; N, number of samples; Min, minimum; Max, maximum; Med, median]

Water-quality station number	USGS station name	N	Total nitrogen			Nitrate			Total phosphorus			Orthophosphate		
			Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med
1	Mississippi River at Thebes, Illinois (Upper Mississippi River)	6	3.1	4.7	3.8	2.07	3.57	2.76	0.24	0.41	0.35	0.07	0.10	0.09
2	Ohio River at Dam 53 near Grand Chain, Illinois (Ohio River)	4	1.3	1.7	1.5	0.94	1.23	0.98	0.058	0.177	0.154	0.022	0.034	0.025
3	Arkansas River at David D Terry Lock and Dam below Little Rock, Arkansas	5	0.76	1.1	0.98	0.23	0.60	0.44	0.087	0.176	0.125	0.035	0.054	0.045
4	Yazoo River below Steele Bayou near Long Lake, Mississippi	9	0.73	1.4	1.25 (N=6)	0.07	1.00	0.41	0.10	0.29	0.18	0.04	0.114	0.061
5	Mississippi River above Vicksburg at mile 438, Mississippi	12	1.6	2.8	2.2	1.09	2.17	1.55	0.15	0.24	0.19	0.05	0.10	0.06
6	Mississippi River near St. Francisville, Louisiana	12	1.6	2.7	2.05	1.11	2.00	1.54	0.14	0.27	0.17	0.05	0.10	0.06
7	Mississippi River at Baton Rouge, Louisiana	6	1.6	2.8	1.95	1.10	1.92	1.44	0.14	0.21	0.16	0.05	0.10	0.06
8	Mississippi River at Belle Chasse, Louisiana	12	1.7	2.8	2.0	1.12	1.97	1.47	0.18	0.27	0.22	0.06	0.12	0.07
9	Atchafalaya River at Melville, Louisiana	12	1.5	2.5	2.1	0.93	1.89	1.51	0.15	0.30	0.19	0.05	0.10	0.07
10	Lower Atchafalaya River at Morgan City, Louisiana	12	1.1	3.1	1.9	0.64	1.57	1.13	0.17	0.34	0.19	0.03	0.11	0.07
11	Wax Lake Outlet at Calumet, Louisiana	11	1.5	2.5	1.8	0.85	1.7	1.17	0.18	0.28	0.20 (N=12)	0.03	0.09	0.06
12	Atchafalaya Floodway near Ramah, Louisiana North of I–10 (Morganza Floodway)	6	0.9	1.6	1.1	0.05	1.03	0.54	0.16	0.52	0.22	0.08	0.43	0.15
13	Bonnet Carré Spillway at US Hwy #61 near Norco, Louisiana (Bonnet Carré Spillway)	7	1.5	1.9	1.7	0.97	1.37	1.13	0.11	0.17	0.16	0.05	0.08	0.06

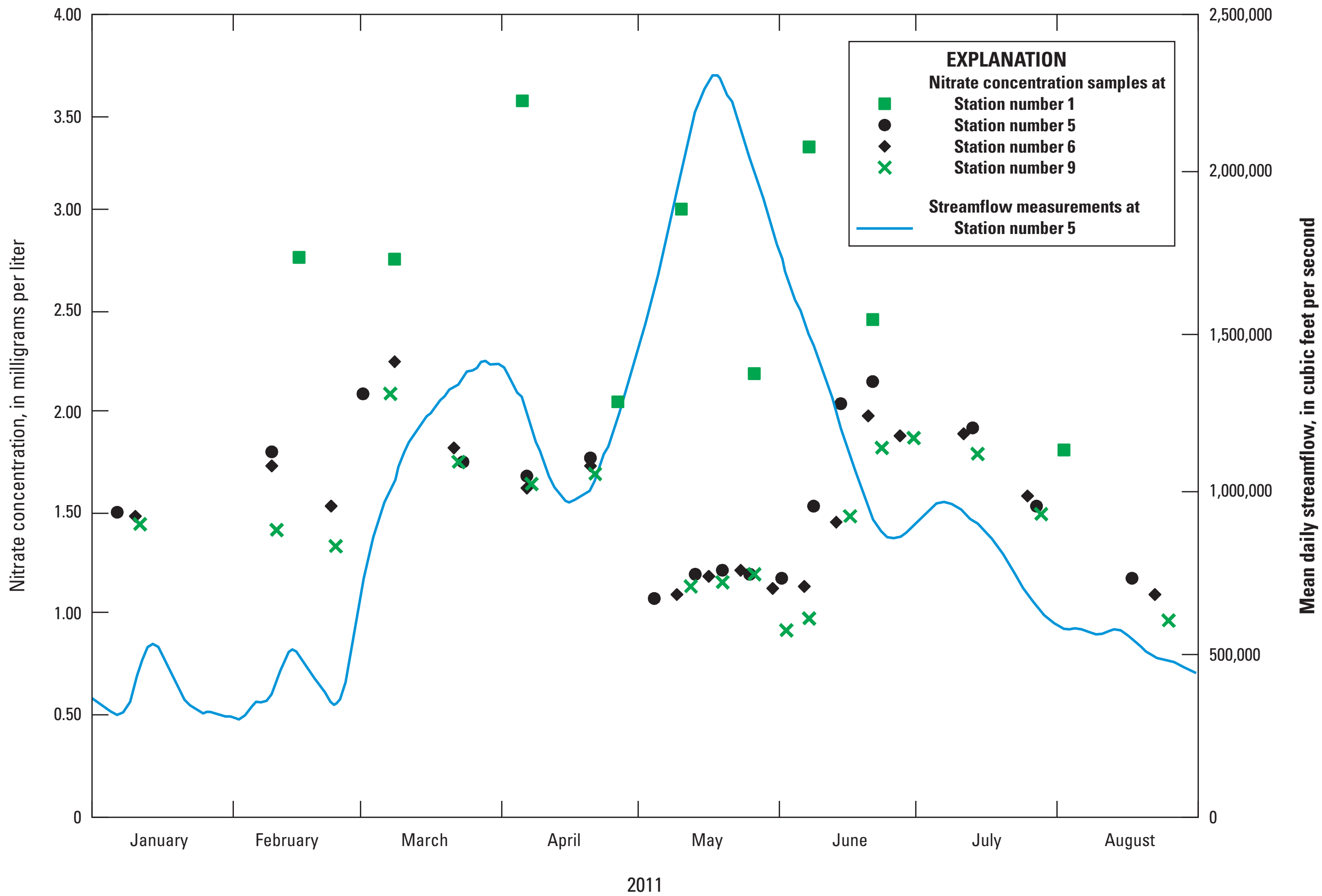

Figure 9. Nitrate concentration in water samples from water-quality station numbers 1, 5, 6, and 9 and streamflow from station number 5 for January–August 2011.

Old River Control Structure and station number 6, although it was <1 percent of the total. The annual nitrate flux in 2011 at station number 6 totaled 770,000 metric tons, which was near the middle range of historical annual fluxes at this site (table 4); 56 percent of the 2011 annual flux occurred during the 2011 flood. Of the nitrate flux at station number 6, 34,970 metric tons (8 percent of the total) was diverted into the Morganza Floodway and Bonnet Carré Spillway (May and June only; fig. 10; table 4).

As the floodwaters moved downstream from the Old River Control Structure into the Atchafalaya River, nitrate flux increased and then decreased with distance. A 9-percent gain in nitrate flux (14,500 metric tons) occurred before the water reached station number 9 (fig. 10). The annual nitrate flux in 2011 at station number 9 (321,000 metric tons) was toward the higher end of historical annual fluxes for that site (table 4); 55 percent of the 2011 annual nitrate flux for the station was from the 2011 flood. Between station number 9 and station numbers 10 and 11, there was 10-percent loss in nitrate flux (17,900 metric tons) (fig. 10; table 4). Chemical reactions occurring between the river water and wetland areas along the Atchafalaya River may have contributed to a small fraction of the total nitrate assimilation for the 2011 flood.

The annual nitrate flux entering the Gulf of Mexico in 2011 was 1.09 million metric tons, which was toward the higher end of the range of historical fluxes (table 4). Approximately half (51 percent) of this flux was delivered to the Gulf of Mexico during the 2011 flood (table 4). When comparing the nitrate flux inputs with the nitrate flux outputs in the lower Mississippi-Atchafalaya River subbasin, 30,570 fewer metric tons of nitrate (5.2 percent) left the subbasin than entered it from the confluence of the upper Mississippi and Ohio Rivers during the 2011 flood (table 4). This small difference in the inputs and outputs (<6 percent) is within the standard error, and nitrate fluxes at stations downstream from the confluence of the upper Mississippi and Ohio Rivers in both the lower Mississippi River and the Atchafalaya River do not seem to have changed substantially (fig. 10). Nitrate appeared to behave conservatively in the lower Mississippi-Atchafalaya River subbasin, which indicates that there was no substantial denitrification or nitrate assimilation occurring in the interior portions of the subbasin before discharging to the Gulf of Mexico (Goolsby and others, 2000).

Table 4. Flux of nitrate and total nitrogen in the lower Mississippi-Atchafalaya River subbasin, April–July 2011.

[All fluxes in metric tons. USGS, U.S. Geological Survey; --, not estimated]

Water-quality station number	USGS station name	Nitrate flux			Total nitrogen flux, 2011 flood
		2011 flood	2011 annual	Historical annual	
Lower Mississippi River stations					
1	Upper Mississippi River	415,000	744,000	111,000–1,200,000[b]	587,000
2	Ohio River	169,500	309,000	183,000–592,000[c]	252,600
5	Vicksburg	590,000	--	--	805,000
6	Saint Francisville	428,700	770,000	237,000–1,240,000[d]	579,000
	Saint Francisville minus the two flood-control structures[a]	393,730	--	--	530,420
Atchafalaya River stations					
9	Melville	178,100	321,000	108,000–403,000[e]	248,300
10	Morgan City	86,600	--	--	129,700
11	Wax Lake	73,600	--	--	105,500
Total flux delivered to the Gulf of Mexico		553,930	1,090,000	507,000–1,330,000[e]	765,620

[a]The two flood-control structures are the Bonnet Carré Spillway and the Morganza Floodway.

[b]For the time period 1973–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[c]For the time period 1963–1970 and 1973–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[d]For the time period 1968–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[e]For the time period 1979–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

Median total phosphorus concentrations measured during the 2011 flood were higher in water from station numbers 1 and 2 than the historical median concentrations at these stations (fig. 11***A***). Conversely, median total phosphorus concentrations measured during the 2011 flood were lower in water from station numbers 6 and 7 than the historical median concentrations at these stations (fig. 11*A*). Flood and historical median concentrations were nearly the same at station numbers 5 and 8 through 11 (fig. 11*A*). Concentrations of total phosphorus at stations 2 through 11 were lower than the total phosphorus concentrations at station number 1 (table 3). Total phosphorus concentrations at station number 5 ranged from 0.15 to 0.24 mg/L with a median concentration of 0.19 mg/L, which is slightly higher than the median concentration at station number 2, indicating a mix of water from the Ohio River with water containing higher total phosphorus concentrations from the upper Mississippi River. Station number 8 was the only station on the lower Mississippi River where the median total phosphorus concentration was higher than the median total phosphorus concentration at station number 5 (table 3). Total phosphorus concentrations in the Atchafalaya River ranged from 0.15 to 0.34 mg/L with a median concentration of approximately 0.2 mg/L at the three stations (table 3). Higher total phosphorus concentrations in water that moved through the Morganza Floodway may have contributed to high total phosphorus concentrations measured at station numbers 10 and 11 (table 3).

Median orthophosphate concentrations in water from samples collected during the 2011 flood were higher at station numbers 2 and 9 through 11 when compared to historical median concentrations at these stations (fig. 11*B*). The median orthophosphate concentration during the 2011 flood was lower than the historical median concentration in water from station numbers 7 and 8, and median orthophosphate concentrations were approximately the same as the historical median concentrations in water from station numbers 1, 5, and 6 (fig. 11*B*).

There was a strong positive correlation ($\rho<0.05$) between total phosphorus and suspended-sediment concentrations at station numbers 1, 2, 4 through 6, and 10 (data not shown). The relation between total phosphorus and

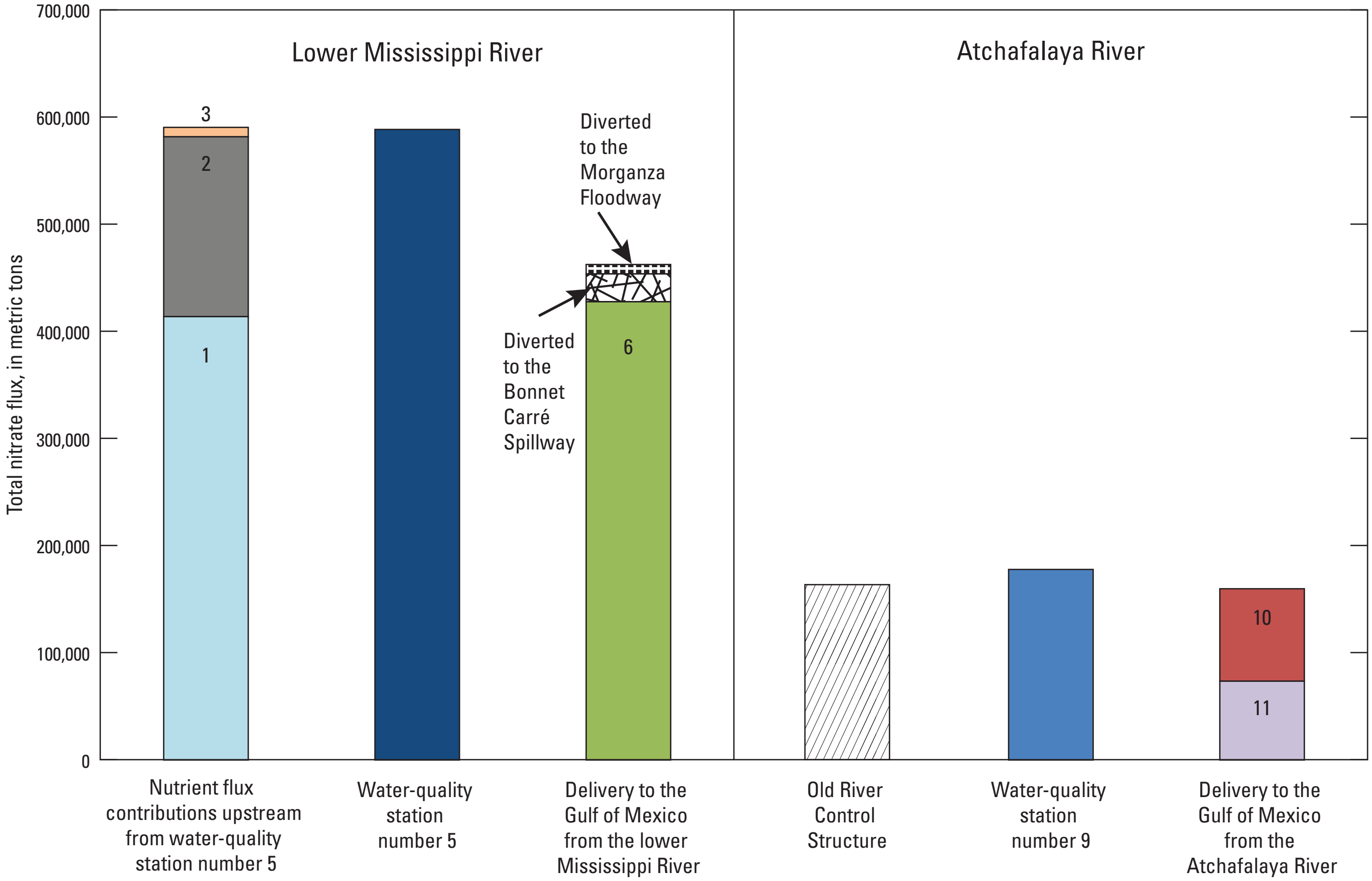

Figure 10. Cumulative nitrate flux in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July. Pattern fills denote a diversion of nitrate flux. Numbers within the bars correspond to the water-quality station numbers in table 1.

suspended-sediment concentration at station numbers 9 and 11 was not statistically significant. At all of these stations, there was a general pattern of low total phosphorus concentrations during peak streamflow corresponding with low suspended-sediment concentrations. As streamflow decreased, overall total phosphorus concentrations increased, probably because of an influx of sediment from agricultural fields that had been inundated by floodwater and water from tributaries in backwater during peak streamflow that returned to the Mississippi River after the stage receded. In addition, the percentage of orthophosphate contributing to the total phosphorus concentration increased (fig. 12), which could be the result of poorly oxygenated water from areas in backwater and in floodways releasing sediment-bound phosphorus into solution. As an example, suspended-sediment and total phosphorus concentrations were higher prior to maximum streamflow in late May at station numbers 9 through 11 (fig. 12, suspended-sediment data not shown). After the flood peak and as water receded, total phosphorus concentrations declined and then increased in July. The percentage of orthophosphate contributing to the total phosphorus concentration at station numbers 10 and 11 was influenced by water entering the Atchafalaya River through the Morganza Floodway. Total phosphorus concentrations measured in the floodway were composed of 45- to 82-percent orthophosphate during the time that it was in operation. The release of sediment-bound phosphorus under low-oxygen conditions is probably the cause of the increase in percentage of orthophosphate at station numbers 10 and 11 in mid- to late June. Total phosphorus concentrations increased at all Atchafalaya River stations (9 through 11) in July, which corresponded with an increase in suspended-sediment concentrations as water from tributaries and floodwater from agricultural lands entered the Atchafalaya River as the river stage fell.

Recently, phosphorus has been identified along with nitrate as a contributor to hypoxia in the Gulf of Mexico (Scavia and Donnelly, 2007). The total phosphorus flux that entered the lower Mississippi River from the upper Mississippi River during the 2011 flood was almost 2.5 times more than the total phosphorus flux from the Ohio River (table 5; fig. 13). The annual total phosphorus flux from station number 1 in 2011 was toward the upper end of the estimated historical fluxes (table 5), and the total phosphorus flux of 57,300 metric tons during the 2011 flood was 40 percent of the 2011 annual flux (table 5). At station number 2, the 2011 total phosphorus flux (53,400 metric tons) was also near the

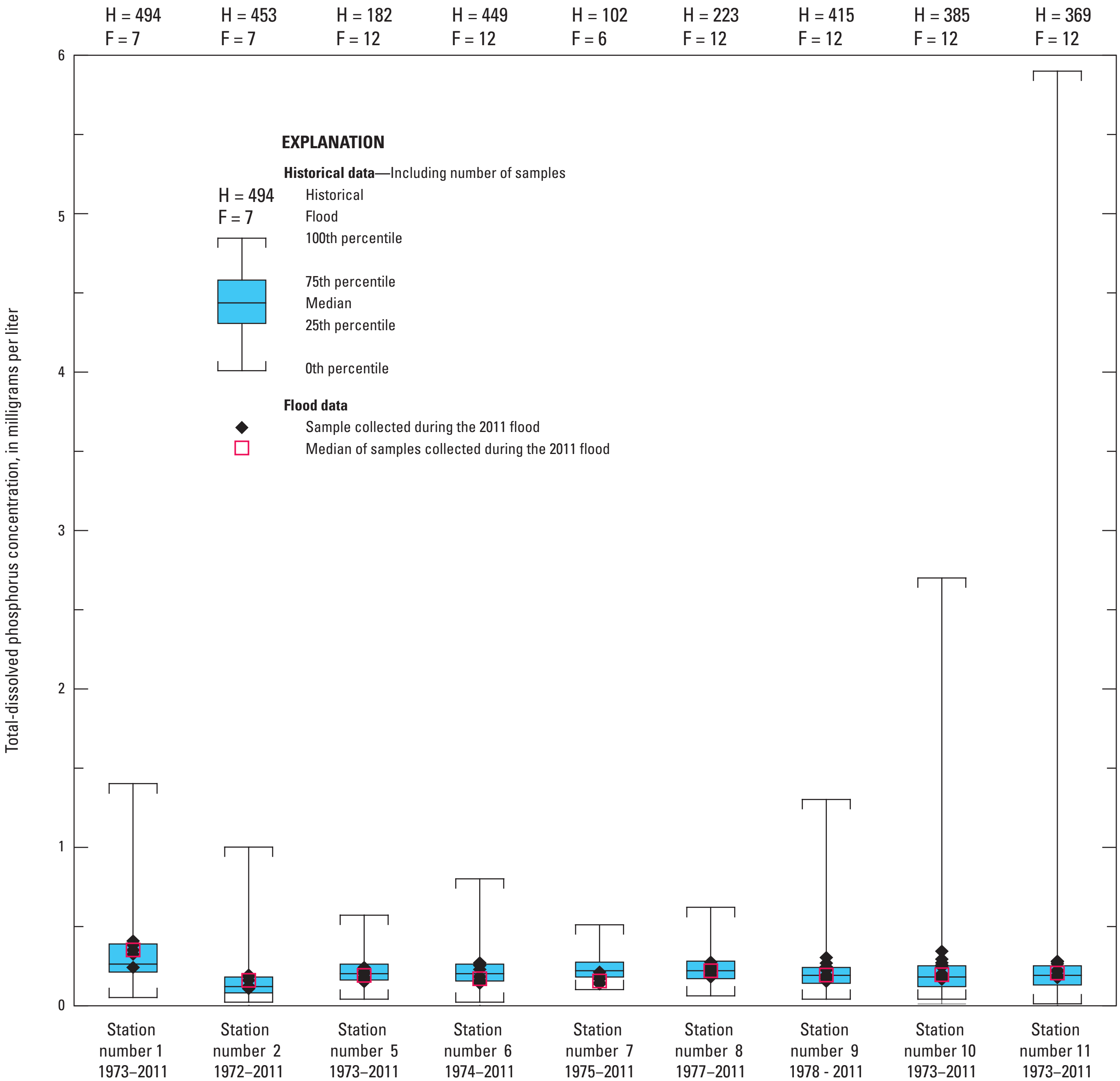

Figure 11. Concentrations of *A*, total phosphorus, and *B*, orthophosphate measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record.

middle range of estimated historical annual fluxes (table 5). The 2011 flood total phosphorus flux of 23,540 metric tons from station number 2 was 44 percent of the 2011 annual flux (table 5; fig. 13).

Another 2,633 metric tons of total phosphorus was delivered to the lower Mississippi River from station number 3. Between the confluence of the upper Mississippi and Ohio Rivers and station number 5, there was a 9-percent loss in total phosphorus (7,540 metric tons) during the 2011 flood. In May 2011, the Yazoo River was in backwater, which accounted for a 120-metric-ton loss of total phosphorus flux in the lower Mississippi River above station number 5. Despite the loss, the estimated total phosphorus flux at station number 5 (73,300 metric tons) was larger than the flux at any other water-quality station during the 2011 flood (table 5; fig. 13). Below station number 5, 28 percent of the flux (20,700 metric tons) was diverted through the Old River Control Structure into the Atchafalaya River (fig. 13). Despite the diversion of

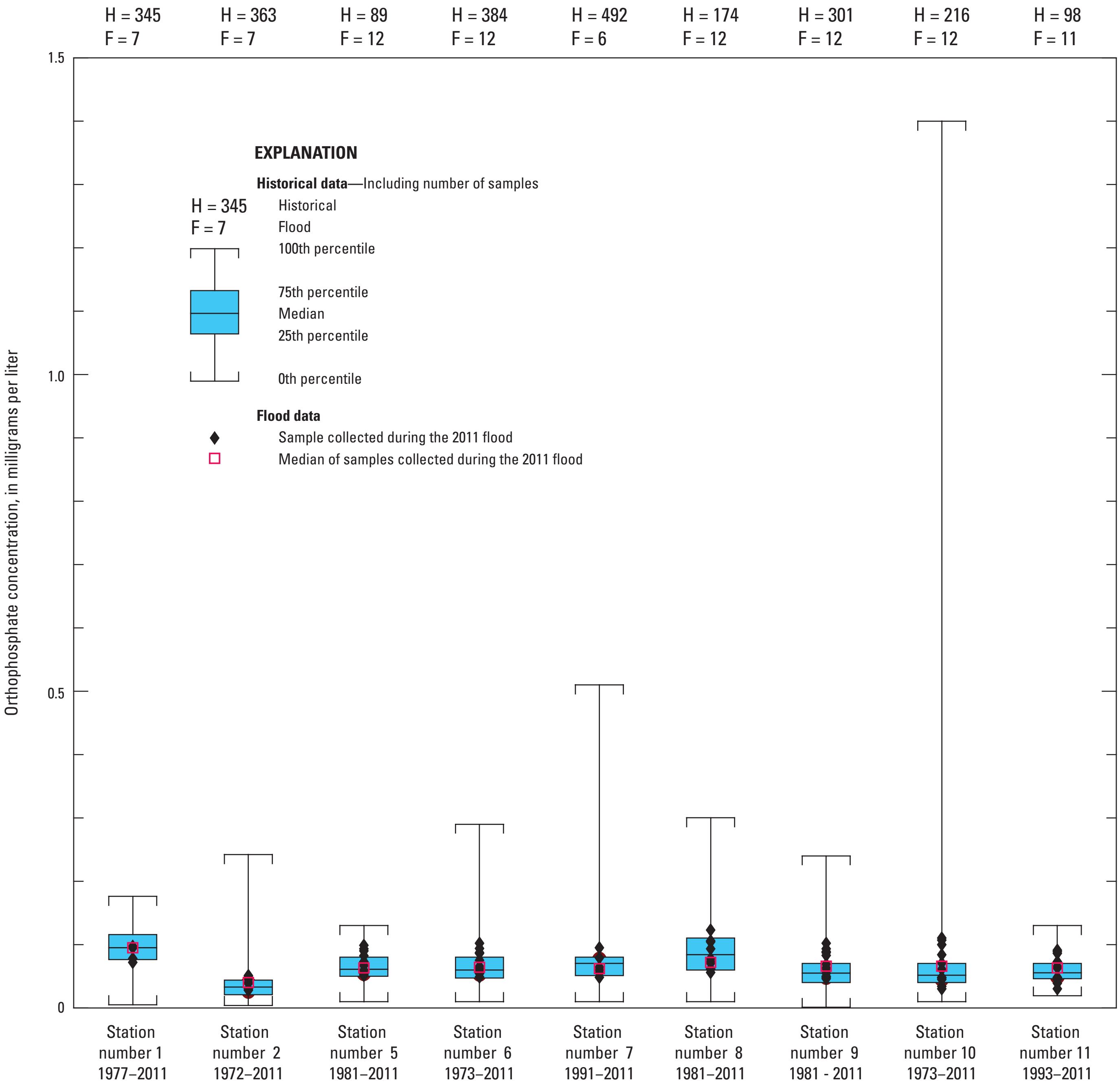

Figure 11. Concentrations of *A*, total phosphorus, and *B*, orthophosphate measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record.—Continued

total phosphorus flux to the Atchafalaya River, there was a gain of 1,500 metric tons in total phosphorus flux between the Old River Control Structure and station number 6. The annual 2011 total phosphorus flux at station number 6 (110,000 metric tons) was in the middle range of historical fluxes (table 5); 49 percent of the 2011 annual flux occurred during the 2011 flood. Below station number 6, approximately 8 percent of the flux (4,390 metric tons) was diverted into the Morganza Floodway and the Bonnet Carré Spillway (May and June only; fig. 13; table 5).

As flood waters moved through the Old River Control Structure into the Atchafalaya River, a 24-percent gain (5,030 metric tons) in total phosphorus flux occurred before the water reached station number 9 (fig. 13). The 2011-flood total-phosphorus flux at station number 9 was 25,730 metric tons (fig. 13; table 5), which was 54 percent of the 2011

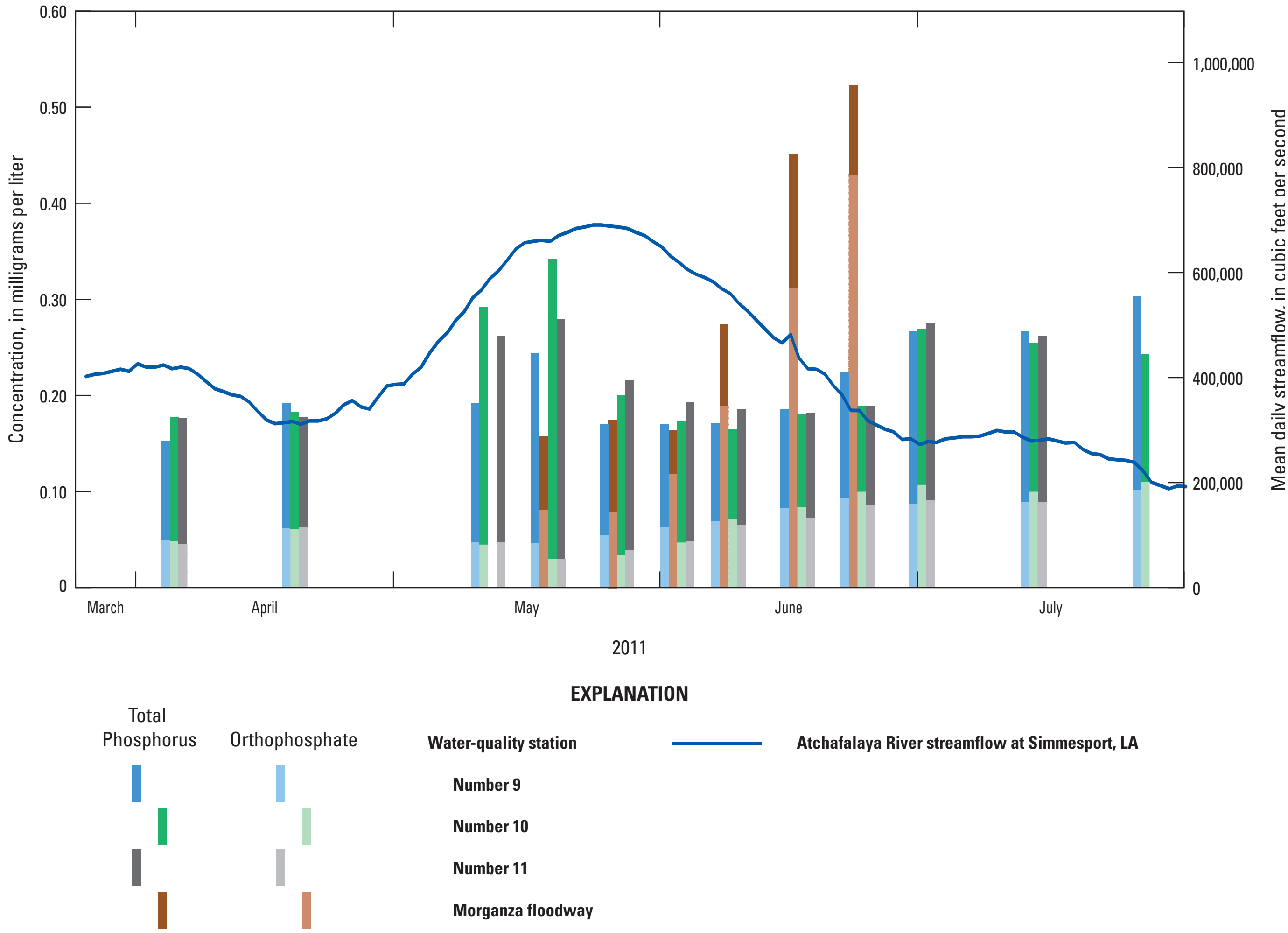

Figure 12. Time-series data of total phosphorus and orthophosphate concentrations in the Morganza Floodway and at three stations on the Atchafalaya River during the 2011 flood. The bar for orthophosphate concentration represents its portion of the total phosphorus concentration at each station.

annual total phosphorus flux (47,400 metric tons). Between station number 9 and station numbers 10 and 11, there was a 16-percent gain in total phosphorus flux (4,020 metric tons) (fig. 13; table 5). Gains in total phosphorus flux between the stations on the Atchafalaya River coincided with gains in suspended-sediment flux along the Atchafalaya River.

The annual total phosphorus flux entering the Gulf of Mexico for 2011 (162,000 metric tons) was near the higher end of the range of historical fluxes (table 5). Forty-nine percent of the 2011 flux was delivered to the Gulf of Mexico during the 2011 flood (79,460 metric tons; table 5). When comparing the total phosphorus flux inputs with the total phosphorus flux outputs for the 2011 flood, 1,380 fewer metric tons of total phosphorus (1.7 percent) left the lower Mississippi-Atchafalaya River subbasin than entered it at the confluence of the upper Mississippi and Ohio Rivers (table 5). Similar to the difference between the input and output of nitrate flux, the small difference between inputs and outputs (<2 percent) in total phosphorus flux is within the standard error. Although there were significant gains in total phosphorus flux along the Atchafalaya River, total phosphorus appeared to behave conservatively in the lower Mississippi-Atchafalaya River subbasin as a whole during the 2011 flood.

The orthophosphate flux that entered the lower Mississippi River from the upper Mississippi River during the 2011 flood was almost 2.5 times more than the orthophosphate flux from the Ohio River (fig. 14). The annual 2011 orthophosphate flux from station number 1 was at the upper end of the range of historical fluxes (table 5); the orthophosphate flux during the 2011 flood (14,800 metric tons) was 44 percent of the 2011 annual flux (table 5). At station number 2, the 2011 orthophosphate flux was 11,400 metric tons, and 54 percent of the annual flux was delivered during the 2011 flood (table 5).

Another 859 metric tons of orthophosphate was delivered to the lower Mississippi River from station number 3. Between the confluence of the upper Mississippi and Ohio Rivers

Table 5. Flux of phosphorus and orthophosphate in the lower Mississippi-Atchafalaya River subbasin, April–July 2011.

[All fluxes in metric tons. USGS, U.S. Geological Survey; --, not estimated]

Water-quality station number	USGS station name	Total phosphorus flux			Orthophosphate flux		
		2011 flood	2011 annual	Historical annual	2011 flood	2011 annual	Historical annual
Lower Mississippi River stations							
1	Upper Mississippi River	57,300	144,000	30,600–186,000[b]	14,800	34,000	12,100–43,900[g]
2	Ohio River	23,540	53,400	17,000–83,100[c]	6,200	11,400	5,580–24,200[h]
5	Vicksburg	73,300	--	--	25,780	--	--
6	Saint Francisville	54,100	110,000	52,400–154,000[d]	19,650	37,600	13,500–52,500[h]
	Saint Francisville minus the two flood-control structures[a]	49,710	--	--	17,910	--	--
Atchafalaya River stations							
9	Melville	25,730	47,400	20,900–63,800[e]	8,180	15,500	5,420–22,100[e]
10	Morgan City	17,230	--	--	4,900	--	--
11	Wax Lake	12,520	--	--	3,530	--	--
Total flux delivered to the Gulf of Mexico		79,460	162,000	73,200–195,000[f]	26,340	53,100	24,100–65,200[i]

[a]The two flood-control structures are the Bonnet Carré Spillway and the Morganza Floodway.

[b]For the time period 1973–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[c]For the time period 1963–1970 and 1973–2010(Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[d]For the time period 1975–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[e]For the time period 1979–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[f]For the time period 1979–1993 and 1996–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[g]For the time period 1982–1986 and 1996–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[h]For the time period 1982–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

[i]For the time period 1992 and 1996–2010 (Aulenbach and others, 2007; accessed on October 29, 2012, at *http://toxics.usgs.gov/pubs/of-2007-1080/*).

and station number 5, there was a 23-percent gain in orthophosphate flux (4,780 metric tons). The orthophosphate flux at station number 5 was 25,780 metric tons, larger than the flux at any other water-quality station during the 2011 flood (table 5; fig. 14). Below station number 5, 29 percent of the flux (7,460 metric tons) was diverted through the Old River Control Structure into the Atchafalaya River (fig. 14). Despite the diversion of some orthophosphate flux to the Atchafalaya River, there was a gain of 1,330 metric tons (about 7 percent) in orthophosphate flux between the Old River Control Structure and station number 6. Below station number 6, 9 percent of the flux (1,741 metric tons) was diverted into the Morganza Floodway and the Bonnet Carré Spillway (May and June only; fig. 14; table 5).

As flood waters entered the Atchafalaya River through the Old River Control Structure, a 10-percent gain in orthophosphate flux (720 metric tons) occurred before the water reached station number 9 (fig. 14). The 2011-flood orthophosphate flux at station number 9 was 8,180 metric tons (fig. 14; table 5), which was 53 percent of the 2011 annual orthophosphate flux (15,500 metric tons). Between station number 9 and station numbers 10 and 11, there was a 3-percent gain (248 metric tons) in orthophosphate flux during the 2011 flood (fig. 14; table 5). A total of 5,336 metric tons more orthophosphate left the lower Mississippi-Atchafalaya River subbasin than entered it above the confluence of the upper Mississippi and Ohio Rivers (table 5). This 25-percent gain in orthophosphate flux is probably the result of phosphorus being released from sediments in the basin, a phenomenon that occurs when oxygen is depleted.

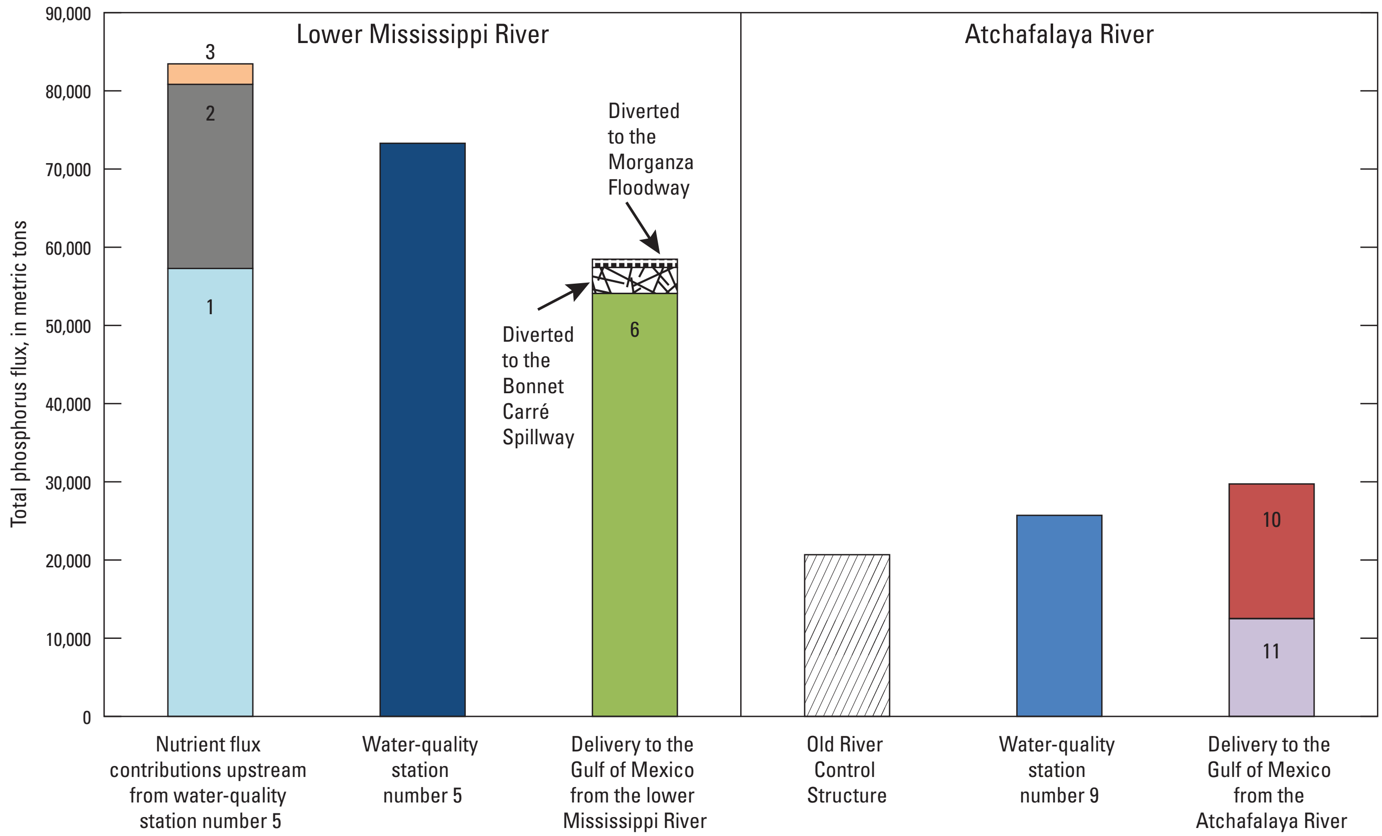

Figure 13. Cumulative total phosphorus flux in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July. Pattern fills denote a diversion of total phosphorus flux. Numbers within the bars correspond to the water-quality station numbers in table 1.

Pesticide Concentrations and Transport

During April–July 2011, water samples collected in the lower Mississippi-Atchafalaya River subbasin were analyzed for 136 pesticides and pesticide degradates. Of the 136 compounds, 118 did not have detections above the method reporting level (table 6). The remaining 18 compounds that had detections above the method reporting level fall into three categories (table 7): (1) compounds that are frequently detected and show a response in concentration to the flood, such as acetochlor, atrazine and its three degradates (deisopropylatrazine, deethylatrazine, and hydroxyatrazine), metolachlor, and simazine; (2) compounds that are detected in nearly every sample at each station but usually in very low concentrations, which include prometon, 2,4–D, alachlor, diuron, 3–4-dichloroaniline, metribuzin, and prometryn (also included in this list because it was frequently detected at all water-quality stations except 1 and 3); and (3) compounds that are infrequently detected, such as the fungicides *cis*-propiconazole, *trans*-propiconazole, and metalaxyl, and the herbicide trifluralin.

Atrazine, Acetochlor, Metolachlor, and Simazine

Four herbicides are among the most commonly used and most frequently detected pesticides in surface and groundwater (Gilliom and others, 2006): atrazine, acetochlor, metolachlor, and simazine. The first three compounds are mainly used in agriculture, although atrazine does have a major non- agricultural use for the control of weeds on residential lawns, highways, and railroad rights-of-way. Simazine is also a commonly used herbicide that has lower total use and higher proportions of non- agricultural use when compared to atrazine, acetochlor, and metolachlor (Gilliom and others, 2006).

Atrazine was detected above the method reporting level in every sample at every station. The highest concentrations were 3.02 and 2.05 µg/L (micrograms per liter) in samples from water-quality station numbers 1 and 2 on May 26 and 31, 2011, respectively. These maximum concentrations occurred well after the peak streamflows during the first week of May at both stations. Concentrations of atrazine remained above 1.0 µg/L at both stations from late May through the third week of June. Atrazine concentrations did not exceed 1.0 µg/L in samples from any other station on the lower Mississippi

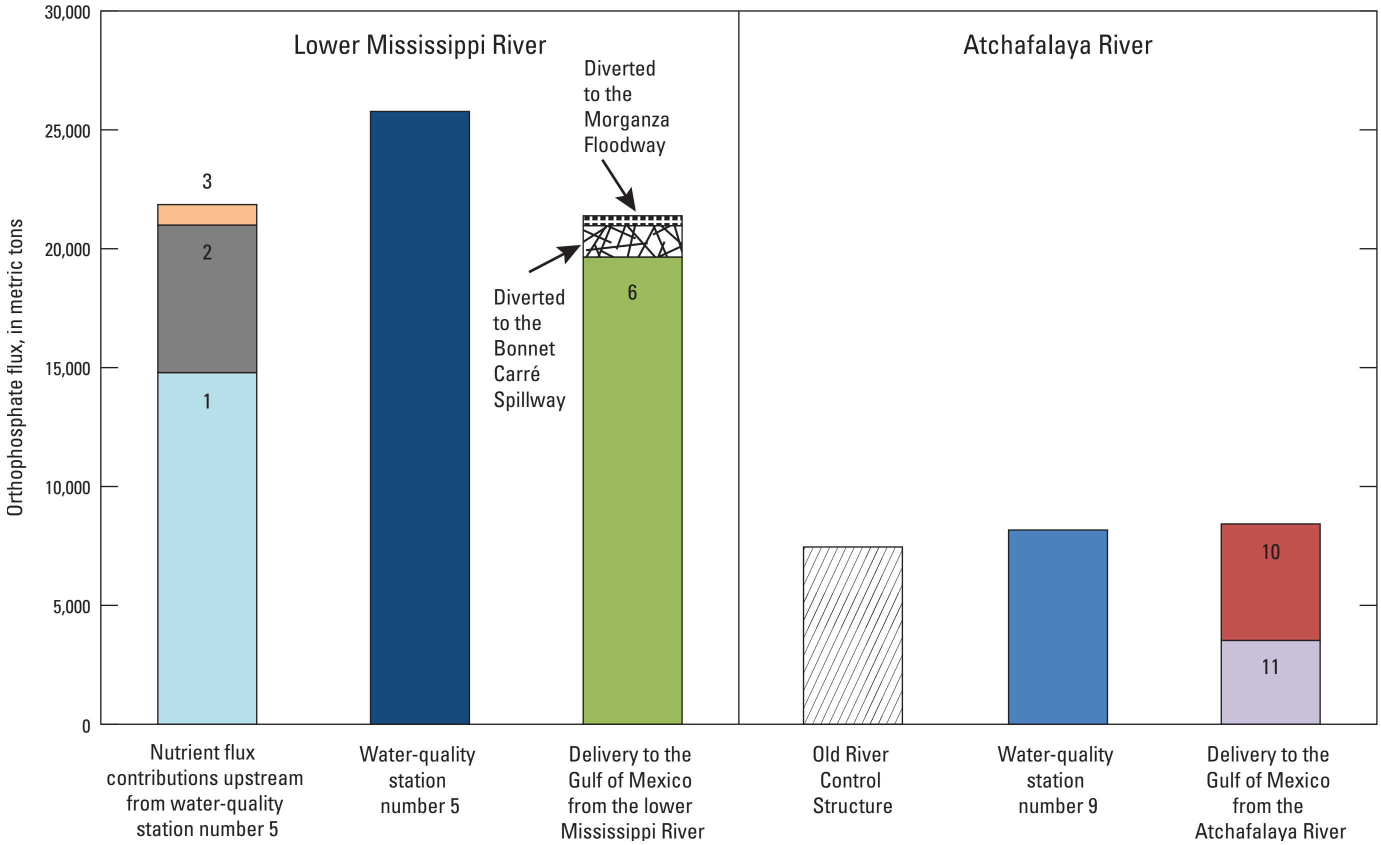

Figure 14. Cumulative orthophosphate flux in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July. Pattern fills denote a diversion of orthophosphate flux. Numbers within the bars correspond to the water-quality station numbers in table 1.

or Atchafalaya Rivers. Concentrations of atrazine at water-quality station number 4 were above 1.0 µg/L beginning in mid-April, reflecting an earlier planting time in the southern part of the Mississippi River Basin.

The deethylatrazine to atrazine ratio (DAR) has been used to indicate the first major runoff event following application of atrazine to corn in the Midwest (Thurman and Fallon, 1996). The DAR has been shown to generally be greater than (>) 0.5 until after application, when it decreases to <0.1. The DAR will slowly increase as the readily available atrazine is depleted through movement offsite or degradation. The first samples from water-quality station numbers 1 and 2 in early April and late March, respectively, had a DAR >0.7, which is indicative of pre-application conditions (fig. 15). The DAR from subsequent samples in late May from both stations had a DAR of about 0.2 or less, indicating that application had begun in the basins and runoff was carrying freshly applied atrazine into the rivers. The DAR remained <0.5 at stations 1 and 2 through the end of sampling in mid-July and late June, respectively. From mid-April through mid-June, the DAR at water-quality station number 4 was 0.2 or less, indicating that application had recently occurred to lands drained by the Yazoo River. The DAR at this station remained <0.5 from late June through July (fig. 15). Three stations on the lower Mississippi River (station numbers 5, 6, and 8) exhibited the same general pattern in DAR throughout the 2011 flood—low DAR during maximum streamflow in the lower Mississippi River and an increase in DAR through most of the falling limb of the flood peak. The DAR was above 0.5 in early June at station number 5 and increased above 0.5 approximately a week later at station numbers 6 and 8, downstream. The ratio fell below 0.5 from late June through July at station numbers 5 and 6; however, at station number 8, the DAR rose above 0.5 again in mid-July before decreasing, which might be the result of tidal influence at this station. This pattern was not captured in data from water-quality station numbers 1 and 2, possibly because of the lower sampling frequency in both rivers. This pattern could also be indicative of another water source with a different DAR, such as tributaries below the confluence of the upper Mississippi and Ohio Rivers entering the lower Mississippi River when streamflow was declining, resulting in dilution of the concentrations in water sampled at water-quality station number 5 and stations farther downstream.

Table 6. List of pesticides not detected in samples from water-quality stations in the lower Mississippi River-Atchafalaya River subbasin, April–July 2011.

[EPTC, S-ethyl-dipropylthiocarbamate; MCPA, 4-chloro-2-methylphenoxyacetic acid; MCPB, 4-4-chloro-2-methylphenoxybutanoic acid; DCPA, Dimethyl tetrachloroterephthalate]

Herbicides			
2,4-D methyl ester	Cycloate	Linuron	Propanil
4-(2,4-dichlorophenoxy)butyric acid	Dicamba	MCPA	Propham
Acifluorfen	Dichlorprop	MCPB	Propyzamide
Benfluralin	Dinoseb	Metsulfuron-methyl	Siduron
Bensulfuron-methyl	Diphenamid	Molinate	Sulfometuron-methyl
Bentazon	EPTC	Neburon	Tebuthiuron
Bromacil	Fenuron	Nicosulfuron	Terbacil
Bromoxynil	Flumetsulam	Norflurazon	Terbuthylazine
Chloramben methyl ester	Fluometuron	Oryzalin	Thiobencarb
Chlorimuron-ethyl	Hexazinone	Oxyfluorfen	Tribuphos
Clopyralid	Imazaquin	Pendimethalin	Triclopyr
Cyanazine	Imazethapyr	Picloram	
Insecticides			
Aldicarb	Diazinon	Fonofos	Phorate
alpha-Endosulfan	Dichlorvos	Imidacloprid	Phosmet
Azinphos-methyl	Dicrotophos	Isofenphos	Propargite
Bendiocarb	Dieldrin	Lambda-cyhalothrin	Propoxur
Carbaryl	Dimethoate	Malathion	Tefluthrin
Carbofuran	Disulfoton	Methidathion	Terbufos
Chloropyrifos	Ethion	Methiocarb	
cis-Permethrin	Ethoprop	Methomyl	
Cyfluthrin	Fenamiphos	Methyl parathion	
Cypermethrin	Fipronil	Oxamyl	
Fungicides			
Benomyl	Myclobutanil	Tebuconazole	
Iprodione	Propiconazole		
Degradates			
1-Napthol	Aldicarb sulfone	Disulfoton sulfone	Malaoxon
2,6-Diethylaniline	Aldicarb sulfoxide	Endosulfan sulfate	Methyl parathion
2-Chloro-2’,6’-diethylacetanilide	Azinphos-methyl oxygen analog	Ethion monoxon	N-(4-Chlorophenyl)-N’-methylurea
2-Ethyl-6-methylaniline	Chlorpyrifos oxygen analog	Fenamiphos sulfone	Phorate oxyen analog
3-Hydroxy carbofuran	DCPA, monoacid	Fenamiphos sulfoxide	Phosmet oxygen analog
3,5-Dichloroaniline	Desulfinylfipronil	Fipronil sulfide	Terbufos oxygen analog sulfone
4-Chloro-3-methylphenol	Desulfinylfipronil amide	Fipronil sulfone	

Table 7. Summary statistics for those pesticides detected in samples from water-quality stations in the lower Mississippi River-Atchafalaya River subbasin at levels above the method reporting level, April–July 2011.

[All concentrations are in micrograms per liter (µg/L). USGS, U.S. Geological Survey; MRL, method reporting level; <, less than]

Pesticide	USGS parameter code	Number of samples	Detection frequency (percent)	MRL	Minimum	Maximum	Median
Herbicides							
2,4-D[a]	39732	35	80	<0.060	<0.060	0.12	0.03
Acetochlor[b]	49260	106	97	<0.010	<0.010	0.474	0.048
Alachlor[a]	46342	106	41	<0.008	<0.008	0.022	<0.008
Atrazine[b]	39632	106	100	<0.008	0.057	3.02	0.49
Diuron[a]	49300	35	100	<0.040	0.020	0.08	0.030
Metolachlor[b]	39415	104	100	<0.020	0.030	2.62	0.22
Metribuzin[a]	82630	106	51	<0.012	<0.012	0.067	0.008
Prometon[a]	04037	106	98	<0.012	<0.012	0.016	0.008
Prometryn[a]	04036	106	75	<0.006	<0.006	0.078	0.007
Simazine[b]	04035	106	100	<0.006	0.015	0.206	0.053
Trifluralin[c]	82661	106	25	<0.018	<0.018	0.034	<0.018
Fungicides							
cis-propiconazole[c]	79846	106	15	<0.008	<0.008	0.11	<0.008
Metalaxyl[c]	61596	106	39	<0.014	<0.014	0.886	<0.014
trans-propiconazole[c]	79847	106	27	<0.010	<0.010	0.12	<0.01
Degradates							
2-Chloro-4-isopropylamino-6-amino-s-triazine (deethylatrazine)[b]	04040	106	100	<0.060	0.024	0.505	0.11
2-Chloro-6-ethylamino-4-amino-s-triazine (deisopropylatrazine)[b]	04038	35	97	<0.060	<0.060	0.14	0.05
2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine (hydroxyatrazine)[b]	50355	35	100	<0.060	0.078	0.317	0.141
3,4-Dichloroaniline[a]	61625	106	87	<0.004	<0.004	0.066	0.005

[a]Compounds that were detected in nearly every sample from each site, but in very low concentrations.

[b]Compounds that were frequently detected and showed a response in concentration to the flood.

[c]Compounds that were infrequently detected.

Atrazine concentrations at the sampling stations in the lower Mississippi-Atchafalaya River subbasin during April–July 2011 were within the same range as concentrations measured during April through July historically (fig. 16*A*). The only water-quality station with significantly different mean atrazine concentrations during the 2011 flood compared to historic concentrations was station number 6, where the mean atrazine concentration during the flood was lower than the historic mean concentration. The highest concentrations of atrazine were at water-quality station numbers 1 and 2. Although concentrations of atrazine were higher at station number 1 than at station number 2, the mean concentrations at the two stations were not significantly different from each other. However, mean atrazine concentrations at water-quality station numbers 1 and 2 were significantly different from mean atrazine concentrations at water-quality stations sampled downstream of the confluence of the upper Mississippi and Ohio Rivers during the 2011 flood.

A subset of samples at all water-quality stations were also analyzed for the three most common degradates of atrazine:

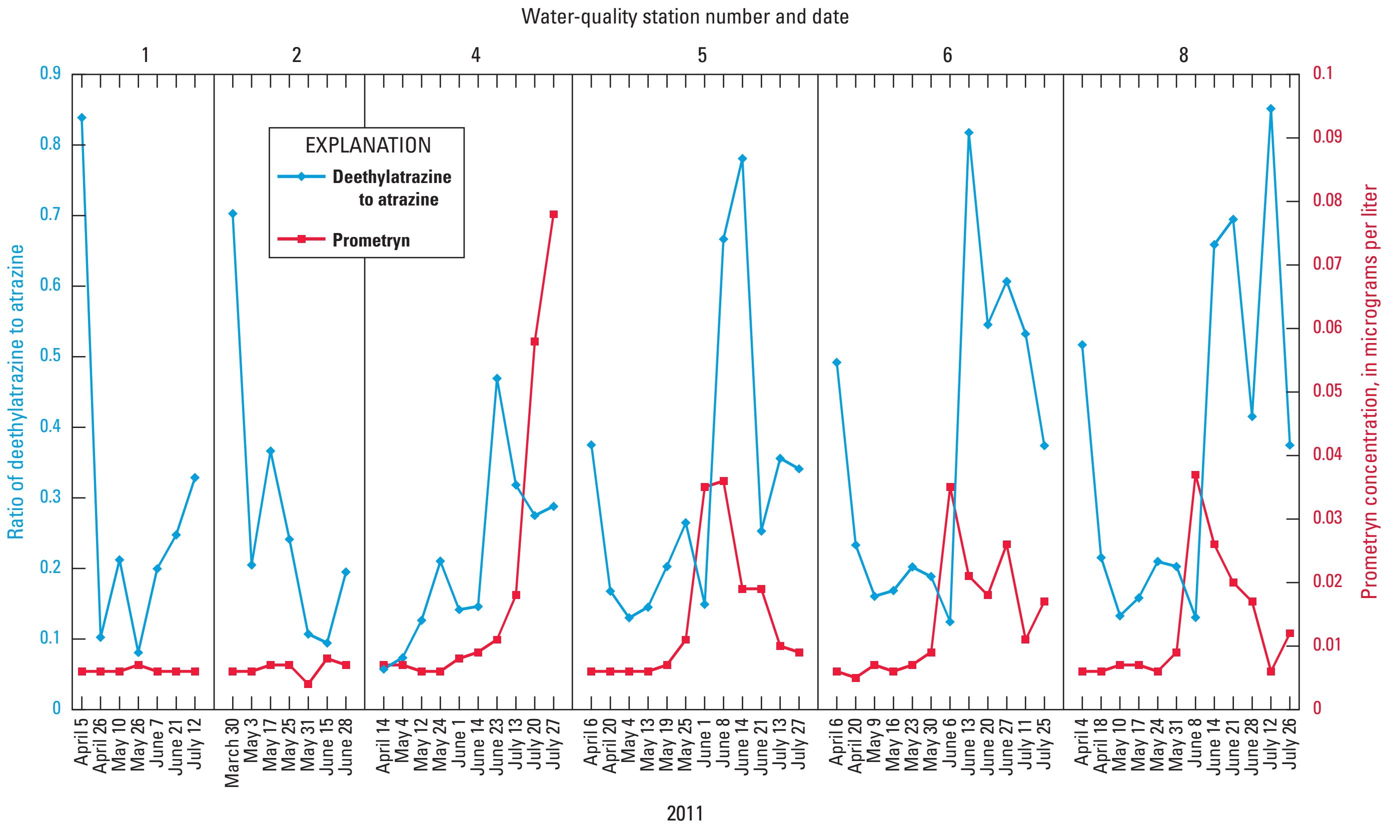

Figure 15. Deethylatrazine to atrazine ratio (DAR) and prometryn concentrations at selected stations on the lower Mississippi River during the 2011 flood, April through July.

deethylatrazine, deisopropylatrazine, and hydroxylatrazine. Total atrazine concentration was calculated for each sampling date at the water-quality stations by summing the degradate concentrations with the parent atrazine concentrations, and then a percentage was calculated to determine the percentage of total atrazine concentration composed of degradates (fig. 17). The total atrazine concentration in water samples from water-quality station numbers 1 and 2 is approximately 20 percent degradates. This percent composition is smaller than the percent composition at stations downstream in the lower Mississippi-Atchafalaya River subbasin. Below the confluence of the upper Mississippi and Ohio Rivers, the three degradates can compose up to 50 percent or more of the total atrazine concentration. This high percentage can be misleading, however, because concentrations of both atrazine and the three degradates are all smaller in the lower Mississippi-Atchafalaya River subbasin, typically <1 µg/L, as compared to station numbers 1 and 2 (concentrations ≥1 µg/L).

Although atrazine has been shown to be conservative in the Mississippi River (Broshears and others, 2001), the flux of atrazine through the lower Mississippi-Atchafalaya River subbasin decreased during the 2011 flood. The total atrazine flux from station numbers 1 and 2 combined for April through July was slightly below 300 metric tons (table 8). Total atrazine flux from station number 5 was 205 metric tons, and from station numbers 6 and 9 combined was 193 metric tons. This decrease represents a flux loss of about one-third along the stretch of river between the confluence of the upper Mississippi and Ohio Rivers and station number 5.

The flux of atrazine from the lower Mississippi-Atchafalaya River subbasin to the Gulf of Mexico from April through August was 296 metric tons in 1991, 160 metric tons in 1992, and 539 metric tons in 1993 (Goolsby and others, 1993a). A major flood occurred in the upper Mississippi River subbasin in the summer of 1993, and the high atrazine flux that year probably represented a worst-case scenario. The flux of atrazine from the lower Mississippi-Atchafalaya River subbasin during April–July 2011 was 193 metric tons, less than half the flux in 1993, but between the fluxes estimated for 1991 and 1992 (table 8). The use of atrazine in the corn belt of the Midwest did not change substantially between 1992 and 2006 (Sullivan and others, 2009); however, it is probable that atrazine use increased after 2006 because of the increased production of corn for biofuels (Thomas and others, 2009). The smaller atrazine flux in 2011 compared to 1993 probably occurred for several reasons: (1) the 1993 flood was centered in the Midwest corn belt, whereas the 2011 flood was, at least initially, from rainfall further south where atrazine use is less than that in the corn belt, (2) the 2011 flood occurred earlier in the year than the 1993 flood and atrazine had probably not

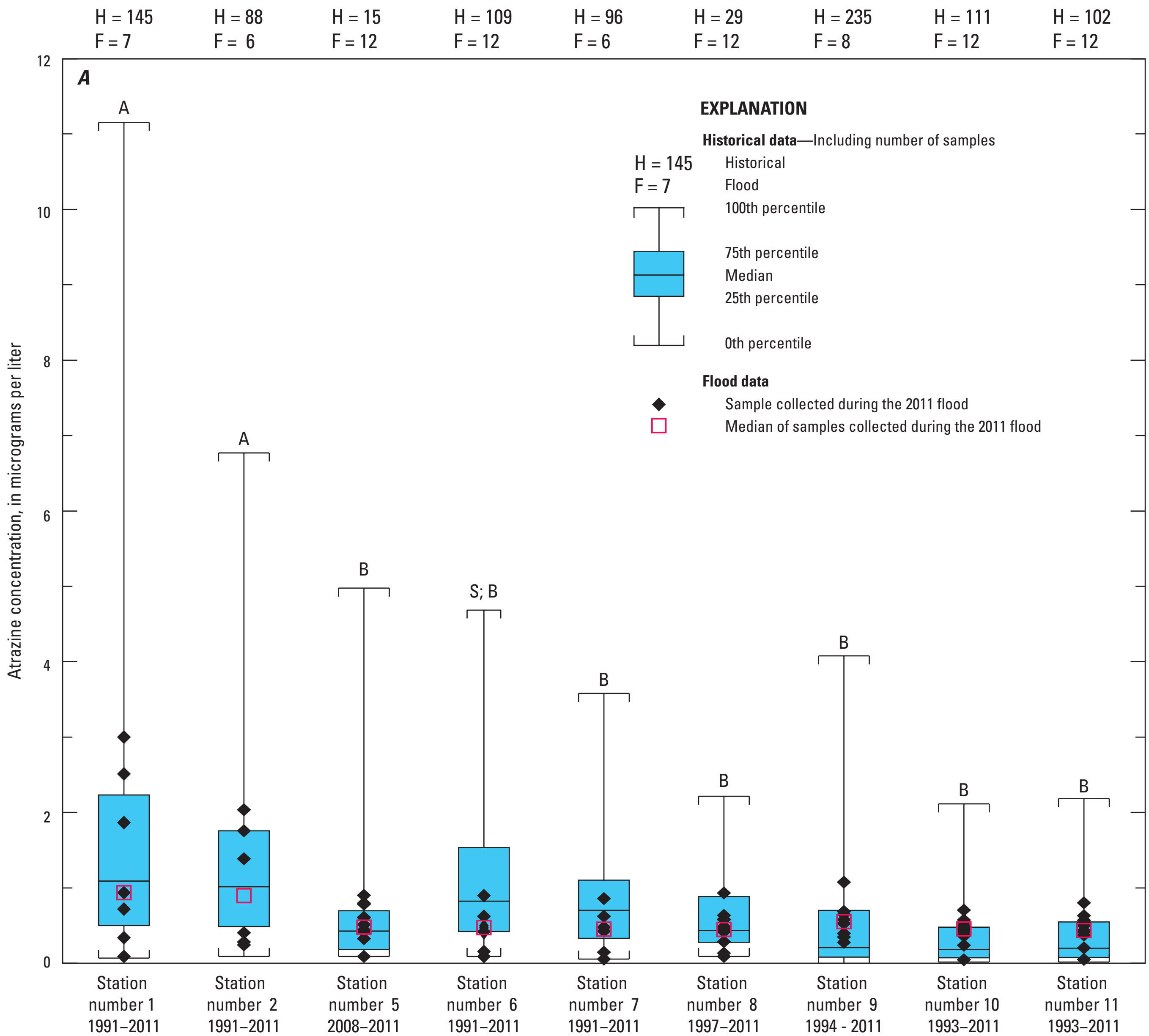

Figure 16. Concentrations of *A*, atrazine, *B*, metolachlor, *C*, acetochlor, and *D*, simazine measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record. S denotes that samples collected during the 2011 flood were significantly different from the April through July historical data at the 95-percent confidence level using the analysis of variance test. Water-quality stations denoted with the same letter (A or B) have 2011 flood concentrations that are not significantly different from one another at the 95-percent confidence level using the parametric test.

been applied on some fields, and (3) the amount of conservation tillage has increased since the 1993 flood, and there have been improvements in how and when atrazine is applied.

Metolachlor was detected above the method reporting level in every sample at every station (table 7). The highest concentrations from water-quality station numbers 1 and 2 were 1.2 and 0.98 µg/L on June 7 and 28, 2011, respectively. Metolachlor concentrations did not exceed 1.0 µg/L at any other station along the lower Mississippi or Atchafalaya Rivers. The mean metolachlor concentration during the study period was higher in water from station number 1 compared to water from the other water-quality stations, but not significantly different than that of any other water-quality station on the lower Mississippi or Atchafalaya Rivers (fig. 16*B*). Concentrations of metolachlor in water from water-quality station number 4 were above 2.0 µg/L for much of June and July. The mean metolachlor concentration at station number 4 was significantly higher than at any other water-quality station in the

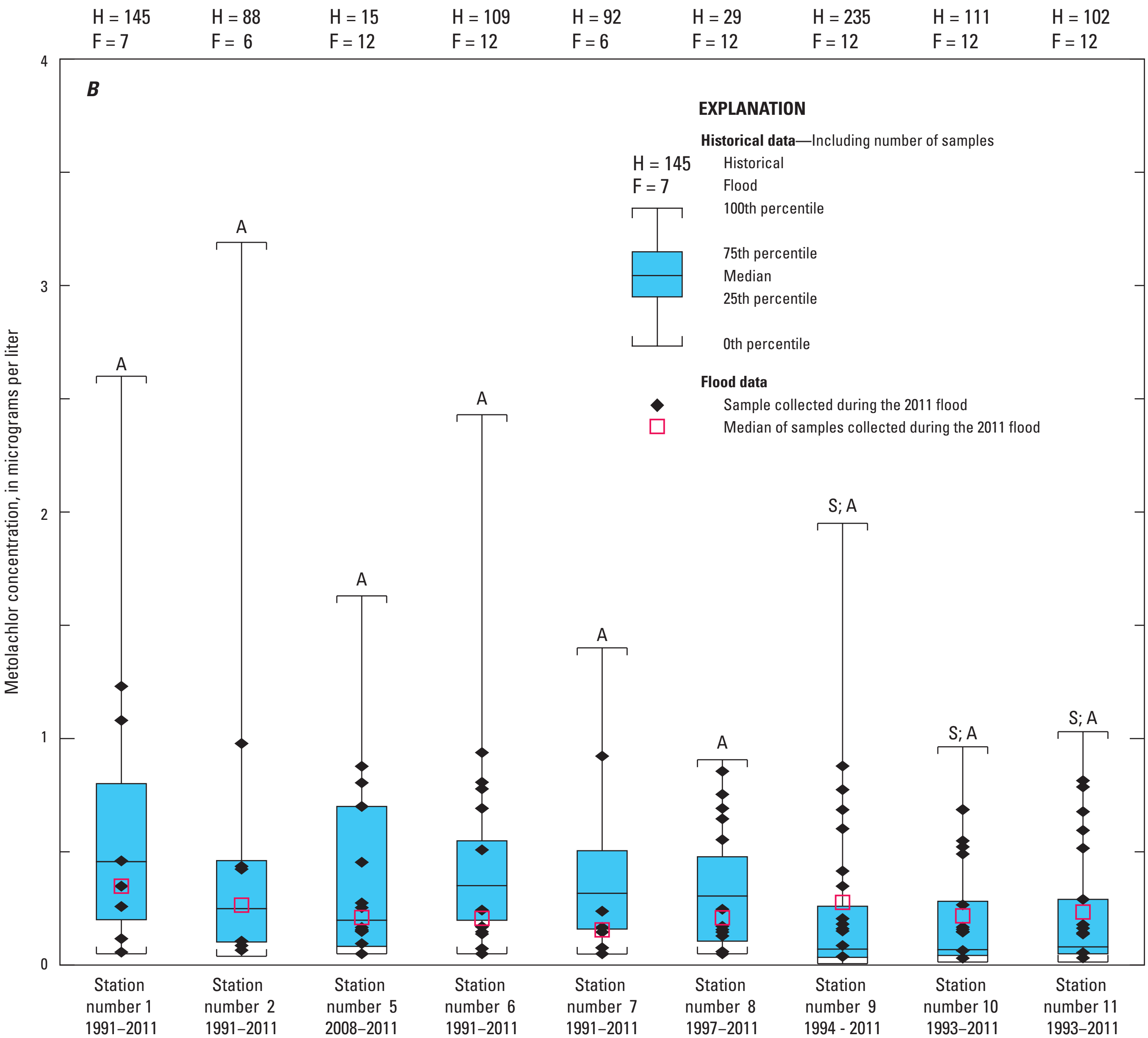

Figure 16. Concentrations of *A*, atrazine, *B*, metolachlor, *C*, acetochlor, and *D*, simazine measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record. S denotes that samples collected during the 2011 flood were significantly different from the April through July historical data at the 95-percent confidence level using the analysis of variance test. Water-quality stations denoted with the same letter (A or B) have 2011 flood concentrations that are not significantly different from one another at the 95-percent confidence level using the parametric test.—Continued

lower Mississippi-Atchafalaya River subbasin (data provided in Welch and Barnes, 2013). Metolachlor can be used on lands planted in soybean and cotton that are drained by the Yazoo River, and these crops have a later planting time than corn.

Compared to historical concentrations of metolachlor at station numbers 1 and 2 and stations on the lower Mississippi River, concentrations during the 2011 flood had a narrower range and distribution, excluding station number 8, and were not significantly different at most water-quality stations (fig. 16*B*). However, the 2011 flood metolachlor concentrations were higher and significantly different from historical concentrations at all three sampling stations (9 through 11) on the Atchafalaya River. This finding could indicate the presence of another source of metolachlor to the Atchafalaya River, possibly the Red River or flooded farmland.

The flux of metolachlor from the lower Mississippi-Atchafalaya River subbasin during April–July 2011 was 136 metric tons (table 8), which was near the lower end of the

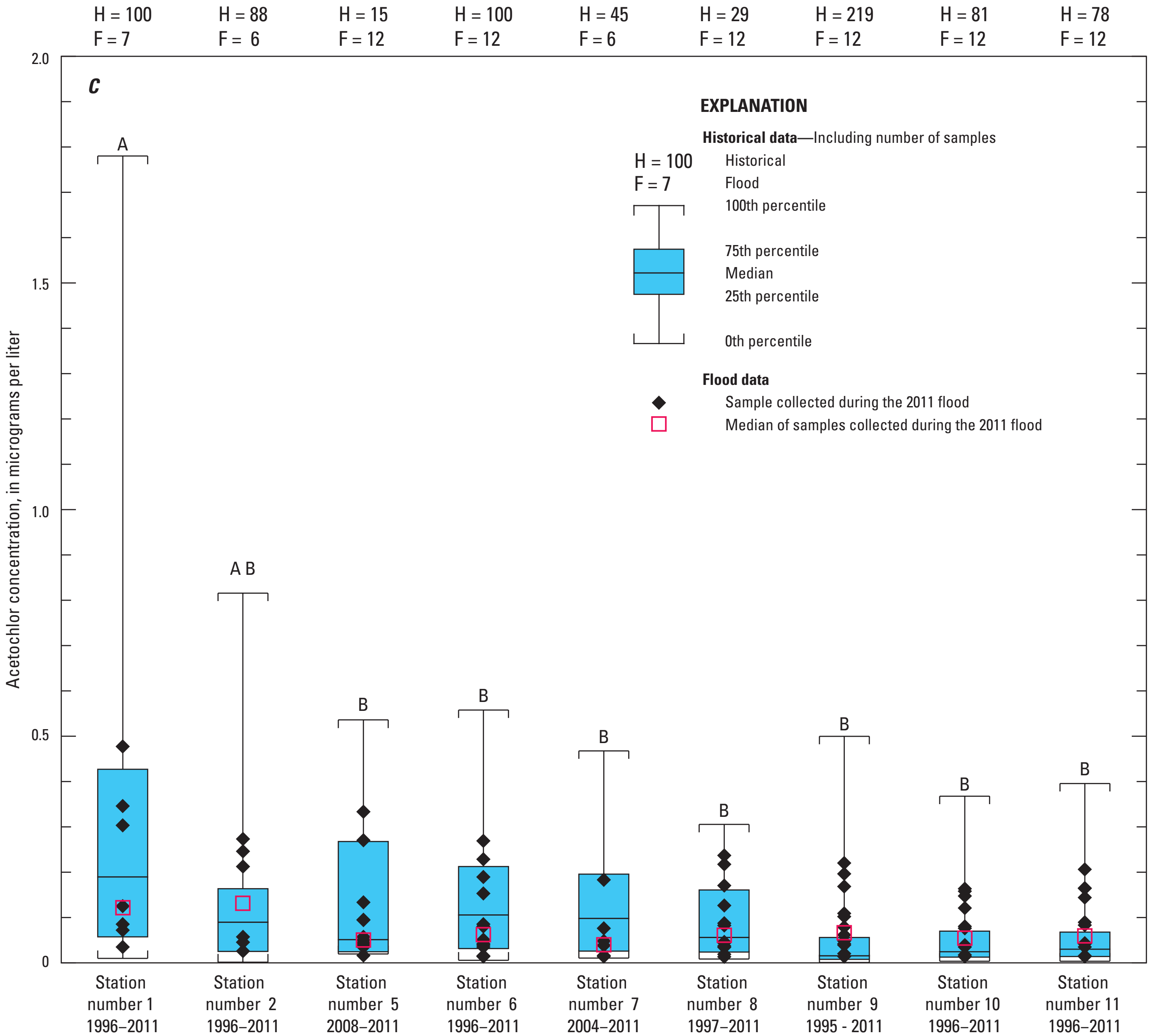

Figure 16. Concentrations of *A*, atrazine, *B*, metolachlor, *C*, acetochlor, and *D*, simazine measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record. S denotes that samples collected during the 2011 flood were significantly different from the April through July historical data at the 95-percent confidence level using the analysis of variance test. Water-quality stations denoted with the same letter (A or B) have 2011 flood concentrations that are not significantly different from one another at the 95-percent confidence level using the parametric test.—Continued

range of historical fluxes (table 8; Kelly and others, 2001). The relatively low concentrations observed during the 2011 flood may be the result of substantially decreased use of metolachlor in the corn belt of the Midwest over time. This decrease may be attributed to the reformulation of the applied product that resulted in lower application rates (Sullivan and others, 2009).

Acetochlor was detected above the method reporting level in almost every water sample from the water-quality stations in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood (table 7). The highest concentration was 0.474 µg/L in water from station number 1 collected on June 7, 2011. The detection frequency and concentrations were less in water samples from station numbers 3 and 4. Compared to historical concentrations of acetochlor, concentrations during the 2011 flood were not significantly different than historical data from the same months (fig. 16*C*). The mean concentrations of acetochlor from station numbers 1 and 2 were significantly higher than the mean concentration at water-quality

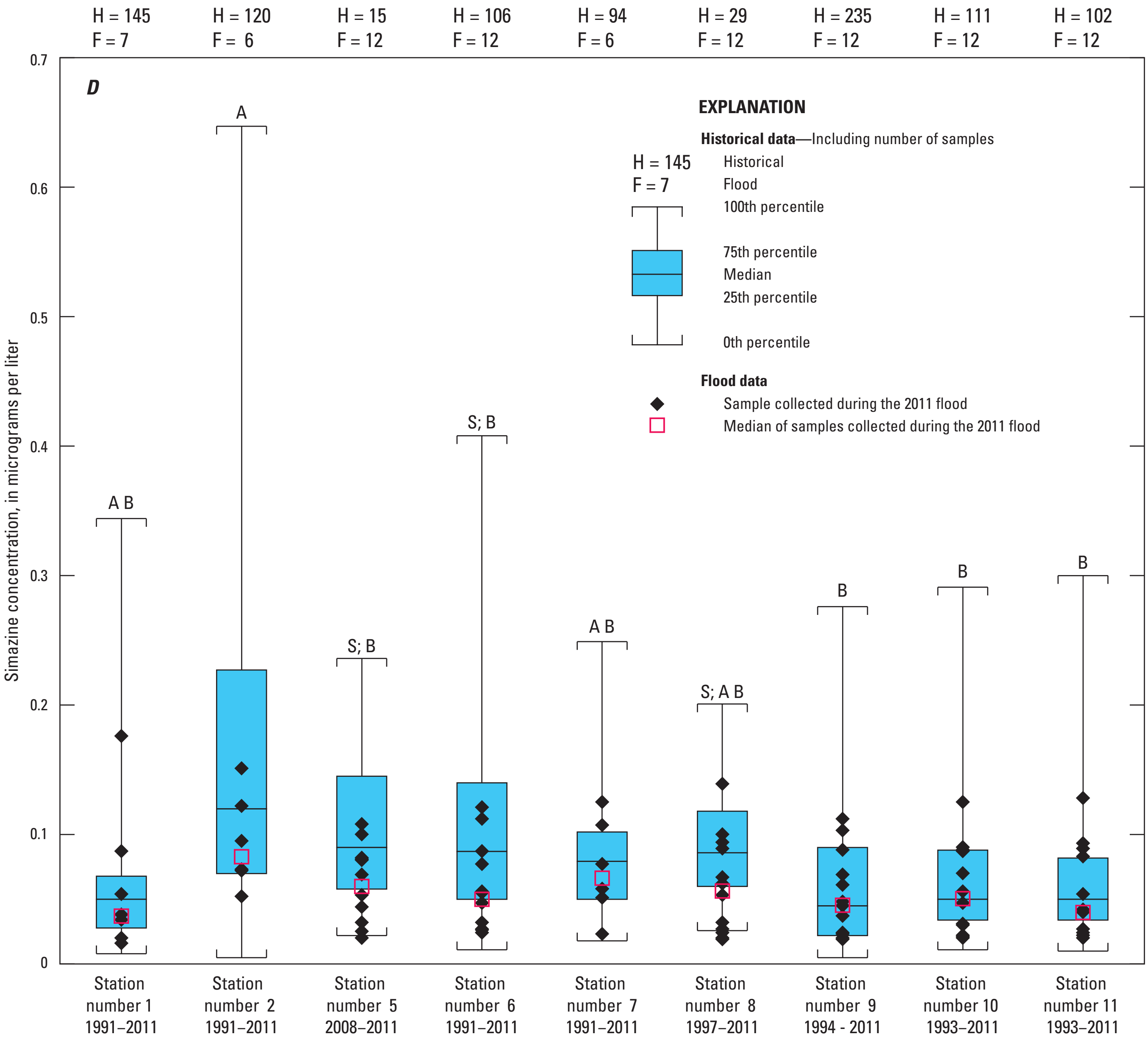

Figure 16. Concentrations of *A*, atrazine, *B*, metolachlor, *C*, acetochlor, and *D*, simazine measured during the flood of 2011 compared to concentrations measured at these stations in the lower Mississippi-Atchafalaya River subbasin for the period of record. S denotes that samples collected during the 2011 flood were significantly different from the April through July historical data at the 95-percent confidence level using the analysis of variance test. Water-quality stations denoted with the same letter (A or B) have 2011 flood concentrations that are not significantly different from one another at the 95-percent confidence level using the parametric test.—Continued

stations in the lower Mississippi-Atchafalaya River subbasin, but mean concentrations at stations 1 and 2 were not significantly different from each during the 2011 flood.

The flux of acetochlor exiting from the Mississippi-Atchafalaya River subbasin during the 2011 flood period was 33 metric tons (table 8). The use of acetochlor in the corn belt of the Midwest was fairly constant between 2000 and 2006 in the upper Mississippi and Ohio River subbasins (Sullivan and others, 2009). Therefore, the estimated 2011 flood flux is within the range of historical fluxes (Kelly and others, 2001).

Simazine was detected in every water sample collected during the 2011 flood period at every water-quality station in the lower Mississippi-Atchafalaya River subbasin (table 7). The highest concentration (0.206 µg/L) was measured in water collected from station number 4 on April 14, 2011. The highest mean simazine concentration during the 2011 flood was from station number 2, but the mean concentration at this

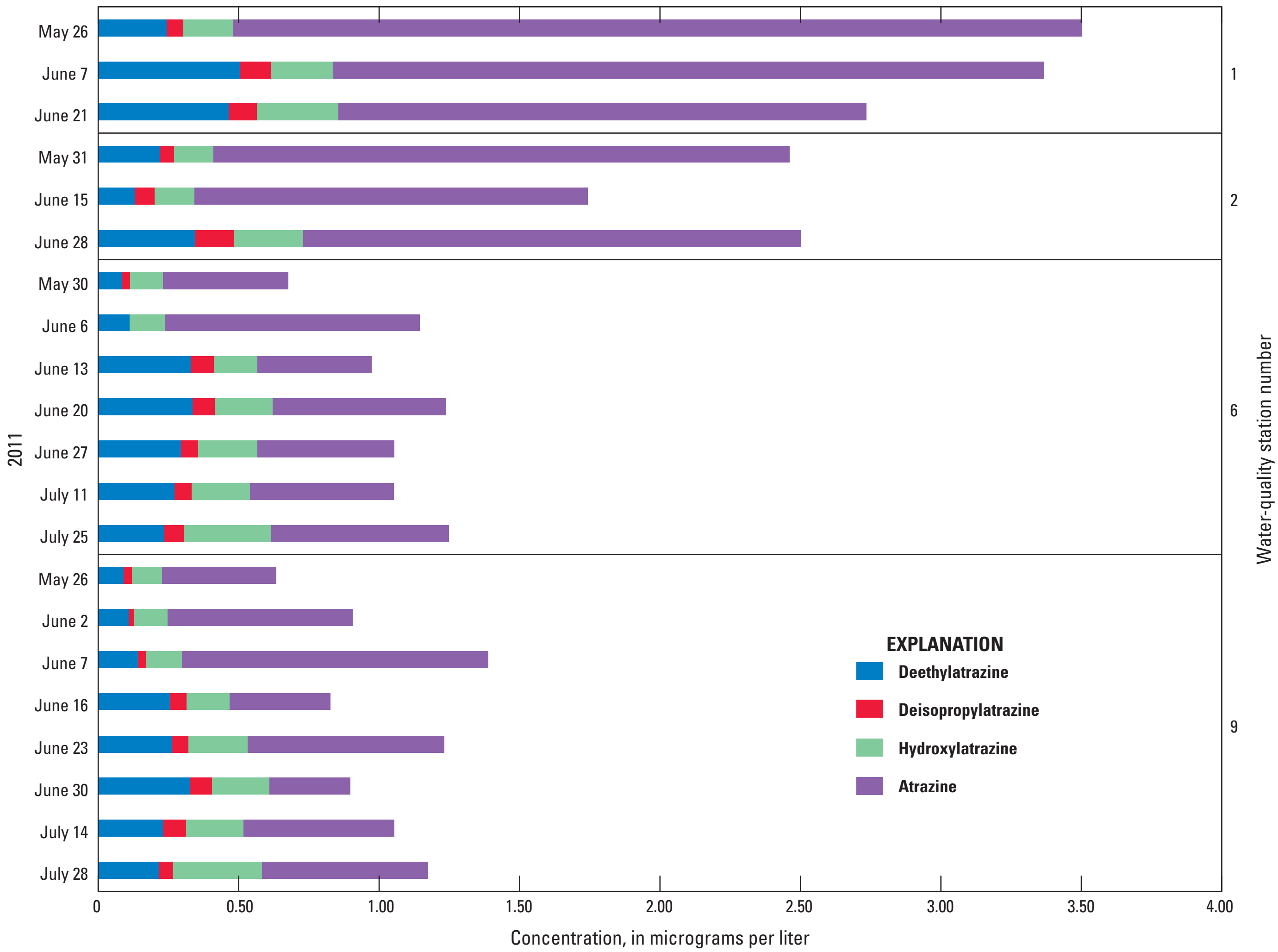

Figure 17. Total atrazine concentration composed of degradates at selected water-quality stations in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July.

station was not significantly different from the mean simazine concentrations at station numbers 1, 7, and 8; historically, simazine concentrations have been higher in water samples from station number 2 (fig. 16*D*). Downstream from the confluence of the upper Mississippi and Ohio Rivers, median simazine concentrations fell between the concentrations measured in water from station numbers 1 and 2. Compared to historical concentrations of simazine (fig. 16*D*) from April through July, concentrations measured during the 2011 flood were significantly lower at station numbers 5, 6, and 8 during the 2011 flood.

The flux of simazine exiting from the Mississippi-Atchafalaya River subbasin during the 2011 flood was 26 metric tons (table 8). The flux of simazine for the 2011 flood was within the range of fluxes estimated between 1996 and 2000 (Kelly and others, 2001). This was expected because the use of simazine in the corn belt of the Midwest did not change substantially between 2000 and 2006 (Sullivan and others, 2009).

Alachlor, Metribuzin, Diuron, 2,4–D, 3,4–Dichloroaniline, Prometon, and Prometryn

The use of the herbicides alachlor and metribuzin has declined substantially since the 1990s (Gilliom and others, 2006; Lerch and others, 2011) because other herbicides, such as acetochlor and glyphosate, are now in use. Both alachlor and metribuzin were frequently detected, in 41 and 51 percent of the water samples collected at stations within the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, respectively (table 7). Neither alachlor nor metribuzin were detected in water samples from station number 3, and alachlor was not detected in water from station number 4 during the 2011 flood. The maximum alachlor concentration measured in water in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood was 0.022 µg/L at station number 2 on May 31, 2011, and the highest metribuzin concentrations was 0.067 µg/L at station number 4 on June 23, 2011.

Table 8. Total 2011 flood fluxes of selected pesticides in the lower Mississippi-Atchafalaya River subbasin during the 2011 flood, April through July.

[All fluxes in metric tons. USGS, U.S. Geological Survey; --, not estimated]

Water-quality station number	USGS station name	Atrazine flux	Acetochlor flux	Metolachlor flux	Simazine flux
Lower Mississippi River stations					
1	Upper Mississippi River	207	30	80	10
2	Ohio River	91	--	30	16
5	Vicksburg	205	32	118	25
6	Saint Francisville	134	24	97	18
Atchafalaya River stations					
9	Melville	59	9	40	8
10	Morgan City	34	5	21	5
11	Wax Lake	25	4	18	3
Total flux delivered to the Gulf of Mexico[a]		193[b]	33[c]	136[d]	26[e]

[a]All historical fluxes from 1996–2000 (Kelly and others, 2001).

[b]Historical flux was 265 to 816 metric tons.

[c]Historical flux was 20 to 63 metric tons.

[d]Historical flux was 77 to 306 metric tons.

[e]Historical flux was 21 to 49 metric tons.

Diuron and 2,4–D are important herbicides used to control weeds in agriculture and urban settings, and 3,4-dichloroaniline is a degradate of diuron, propanil, and other herbicides. Diuron and 2,4–D were analyzed in just a few samples from selected sampling stations. Diuron was detected in all of these samples, with a maximum concentration of 0.08 µg/L found in a sample from station number 1 on May 26, 2011 (table 7); the median concentration of diuron was 0.03 µg/L. 2,4–D was detected in 80 percent of samples (table 7), and most of these detections occurred in samples collected prior to June 23, 2011. The degradate 3,4-dichloroaniline was detected in 87 percent of the samples, generally in very low concentrations (table 7). The median 3,4-dichloroaniline concentration was 0.005 µg/L; the highest concentration was 0.066 µg/L, measured in water from station number 4 at the end of July, probably because of propanil use on rice planted on lands drained by the Yazoo River. There were no concentrations of 3,4-dichloroaniline above the method reporting level of 0.004 µg/L from water collected at station number 2, and no concentrations above 0.01 µg/L, except in samples collected from station number 4.

Prometon is an herbicide registered for non-crop usage only (Gilliom and others, 2006), but it was detected in 98 percent of the samples from the lower Mississippi-Atchafalaya River subbasin (table 7). The concentration range was narrow, with a maximum concentration of 0.016 µg/L, and most detections were below the method reporting level of 0.012 µg/L. There did not appear to be any patterns in the occurrence of prometon among or between samples collected at the water-quality stations. Prometryn is a triazine herbicide and is registered for use on cotton crops. Prometryn was detected above the method reporting level in about 75 percent of the samples; the highest concentration of 0.078 µg/L was from a water sample collected from station number 4 on July 27, 2011 (table 7). There was one water sample from station number 1 with a detection of prometryn, and there were no detections at station number 3. There was no discernible change in concentrations of prometryn detected in water samples from station numbers 1 and 2 (fig. 15). In water samples from station number 5, however, prometryn concentrations increased distinctly about a week after the maximum streamflow was reached in late May, peaked in June, and decreased through July. This pattern is also evident at stations downstream of station number 5, particularly at station numbers 6 and 8. The peak prometryn concentration also corresponds to the spike in DAR at station number 5 and stations farther downstream (fig. 15). Prometryn is only used on cotton in the Mississippi River Basin, and cotton is only grown in the lower Mississippi-Atchafalaya River subbasin. Relative to the upper Mississippi River subbasin, corn is not grown as intensively in the lower

Mississippi-Atchafalaya River subbasin so atrazine is not as widely used there, resulting in relatively high DAR ratios. The spikes in the DAR and in the prometryn concentration suggest that the source is most likely floodwater in agricultural parts of Arkansas and Missouri. The water was held in storage in streams and on land until the stage of the Mississippi River fell enough to allow tributaries that were in backwater to once again flow into the Mississippi River. There are also several smaller river basins where cotton is grown that could have contributed to the spike in prometryn concentrations.

Trifluralin, *cis*- and *trans*-Propiconazole, and Metalaxyl

Trifluralin is a commonly used herbicide, and *cis*- and *trans*-propiconazole and metalaxyl are fungicides. These pesticides were detected at relatively low frequencies in the lower Mississippi-Atchafalaya River subbasin (table 7). Trifluralin was detected in 25 percent of the samples (table 7) with no trifluralin detections at water-quality stations 1 through 3. Most of the detections, all above the method reporting level, of trifluralin and *cis*- and *trans*-propiconazole were measured at station number 4. There were no detections in the lower Mississippi or Atchafalaya Rivers after June 14, 2011; however, trifluralin was detected in water samples from station number 4 in both June and July. An earlier study of fungicides showed that water from the Yazoo River had the highest concentrations and most frequent detections of propiconazole when compared to other streams across the southeastern and midwestern United States (Battaglin and others, 2011). Metalaxyl occurrence was similar to propiconazole occurrence in that the highest detections were from station number 4. Unlike propiconazole, metalaxyl was detected in water from station numbers 1 and 2 in late May and in relatively low concentrations (below the method reporting level) at lower Mississippi River stations after May.

Water Quality in the Morganza Floodway

The Morganza Floodway control structure was open from May 14 to July 7, 2011, diverting streamflow from the Mississippi River above station number 6 to the Atchafalaya River. Inundated land in the basin consists of swamps, small farms, and also contains thousands of oil and gas wells. Consequently, water-quality effects from floodwater flowing from the lower Mississippi River through the floodway into the Atchafalaya River during the 2011 flood were a concern. On average, 66,450 ft^3/s of streamflow was diverted from the lower Mississippi River into the Morganza Floodway for the 55 days that it was in operation. In addition, dissolved oxygen (DO) concentrations in the floodway decreased from 3.7 to 1.4 mg/L from May 27 to June 24 (fig. 18). Changes in DO resulted in reducing conditions that affected nutrient concentrations in the floodway.

Nitrate concentrations in the Morganza Floodway ranged from 0.05 to 1.03 mg/L, with a median concentration of 0.54 mg/L (fig. 18; table 3). There was a general positive relation between DO and nitrate (fig. 18). The highest concentrations of DO and nitrate were measured in May, and concentrations of both constituents decreased with the length of time that the floodway was open. Although no excess nitrogen or isotope samples were collected for analysis, the presence of increasingly reducing conditions, along with a decline in nitrate concentrations, indicates that nitrate processing was occurring in the floodway.

Total nitrogen concentrations in water from the Morganza Floodway ranged from 0.90 to 1.6 mg/L, with a median concentration of 1.1 mg/L; concentrations decreased, given the length of time the floodway was open. The relation between the nitrogen-based compounds that composed the total nitrogen concentration changed throughout the 2011 flood. During the first 3 weeks that the floodway control structure was open, the majority of the total nitrogen concentration was composed of nitrate. As nitrate was assimilated, the concentration of organic nitrogen increased and eventually composed the majority of the dissolved total nitrogen. With length of time that the floodwaters were in contact with the lands in the floodway, reactions between the water and plant material, animal waste, and other organic matter probably contributed to the increase in organic nitrogen concentration.

Two percent of the nitrate flux and 2 percent of the total nitrogen flux estimated at station number 6 for the 2011 flood were diverted through the Morganza Floodway from the lower Mississippi River. Given the downward trend in nitrate concentration with the length of time that the floodway was open, along with the decrease in nitrate flux between station number 9 and station numbers 10 and 11, it can be assumed that the nitrate flux that entered the floodway from the lower Mississippi River was assimilated before the water entered the Atchafalaya River.

Orthophosphate and total phosphorus concentrations increased with the length of time that the Morganza Floodway remained open. Orthophosphate concentrations ranged from 0.08 to 0.43 mg/L, with a median concentration of 0.15 mg/L (table 3). There was a negative relation between DO and orthophosphate: as DO concentrations decreased with the length of time the floodway was open, orthophosphate concentrations increased (fig. 18). Total phosphorus concentrations in water from the Morganza Floodway ranged from 0.16 to 0.52 mg/L, with a median concentration of 0.22 mg/L (table 3). The concentration of total phosphorus was also negatively correlated with DO, although not significantly (ρ-value >0.05, fig. 18). The highest concentrations of orthophosphate and total phosphorus were measured in mid- to late June after the floodway had been in operation over a month. Orthophosphate concentrations composed 45 to 82 percent of the total phosphorus concentration in the floodway, and the percentage of orthophosphate contributing to the total phosphorus

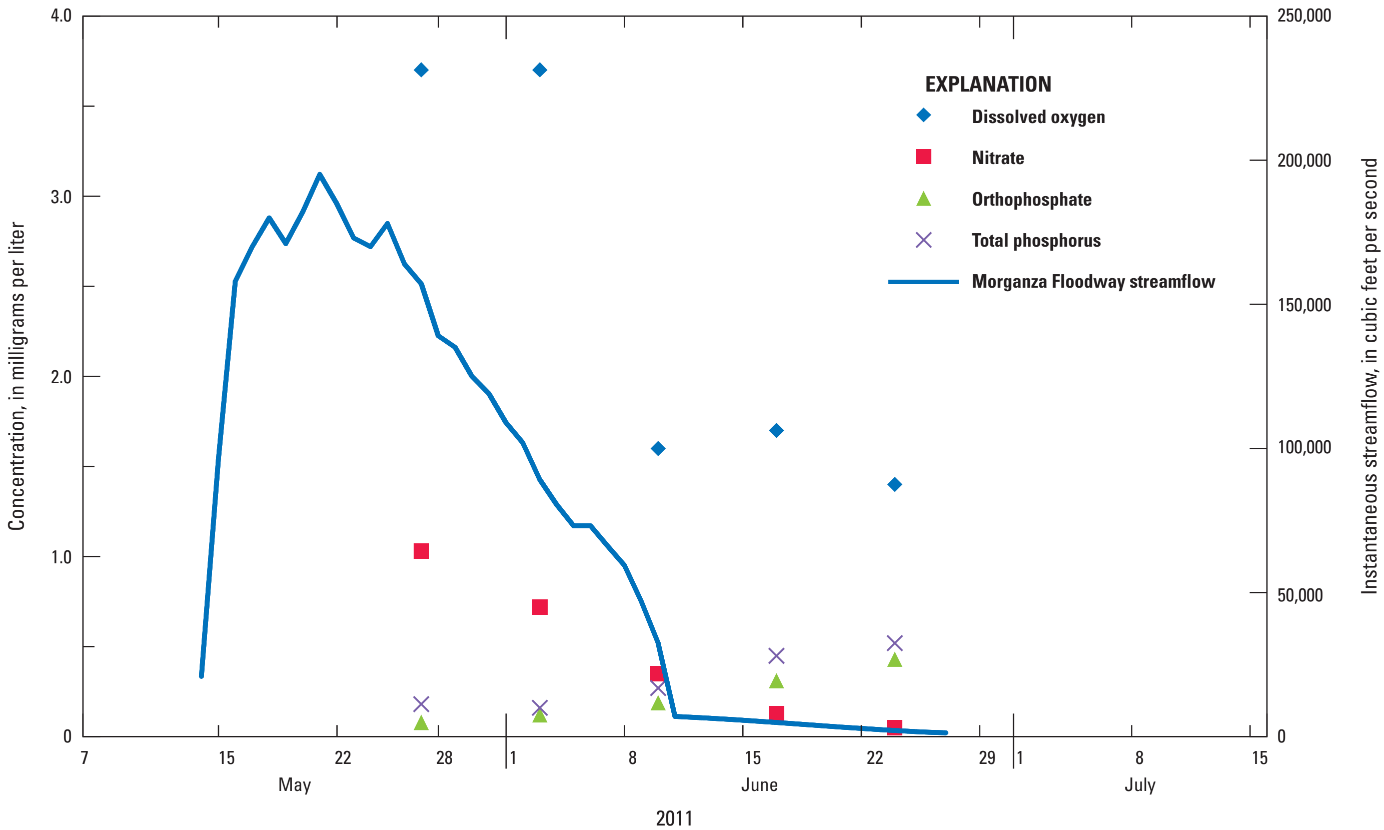

Figure 18. Concentrations of dissolved oxygen, nitrate, orthophosphate, and total phosphorous with streamflow in the Morganza Floodway during the 2011 flood period.

concentration (fig. 12) increased with length of time that the floodway was open. Because suspended-sediment concentrations in the floodway were low (≤31 mg/L), the release of phosphorus bound to suspended sediment was probably not the source of the increase in concentrations of orthophosphate and total phosphorus. Rather, the source was probably the release of phosphorus bound to fine-grained soils inundated by the floodwaters as conditions became reducing (Patrick and Khalid, 1974). Fine-grained particles have high phosphorus sorption capacities (Carlyle and Hill, 2001), resulting in more phosphorus available for desorption.

Two percent of the orthophosphate flux and 2 percent of the total phosphorus flux estimated at station number 6 were diverted through the Morganza Floodway while the gates were open. Median and maximum concentrations of total phosphorus and orthophosphate in the floodway were higher than concentrations of those two constituents at station numbers 9 through 11 on the Atchafalaya River (table 3). Total phosphorus and orthophosphate fluxes increased between station number 9 and station numbers 10 and 11, which may have been a result of flux contributions from water that was diverted through the Morganza Floodway.

Water samples were analyzed for evidence of contaminants from oil and gasoline at station number 9 (hereafter referred to as upstream), and station number 10 (hereafter, referred to as downstream) from May 19 through June 29, 2011, while the Morganza Floodway was in operation. One low-level detection of diesel was measured during the week of May 23 in water upstream from the Morganza Floodway. There were no detections of petroleum hydrocarbons in any samples collected upstream or downstream from the Morganza Floodway. There were 2 detections of gasoline in water upstream and 1 detection in water downstream. Gasoline concentrations were twice as high in the downstream sample as in the upstream sample the week of May 23; the following week, however, gasoline concentrations were twice as high in the upstream sample as in the downstream sample. Oil and grease were detected in every sample upstream and downstream of the outlet. For perspective, McGee (2003) found no detections of oil and grease (method reporting level=5 mg/L) in water from streams located in northeastern Louisiana, and in stormwater runoff in California, typical oil and grease concentrations were generally ≤5 mg/L and seldom exceeded 10 mg/L (California Department of Environmental Quality, 2006). All concentrations in water upstream and downstream from the Morganza Floodway outlet were <5 mg/L. Oil and grease concentrations upstream ranged from 2.0 to 3.5 mg/L with a median concentration of 2.2 mg/L, and concentrations

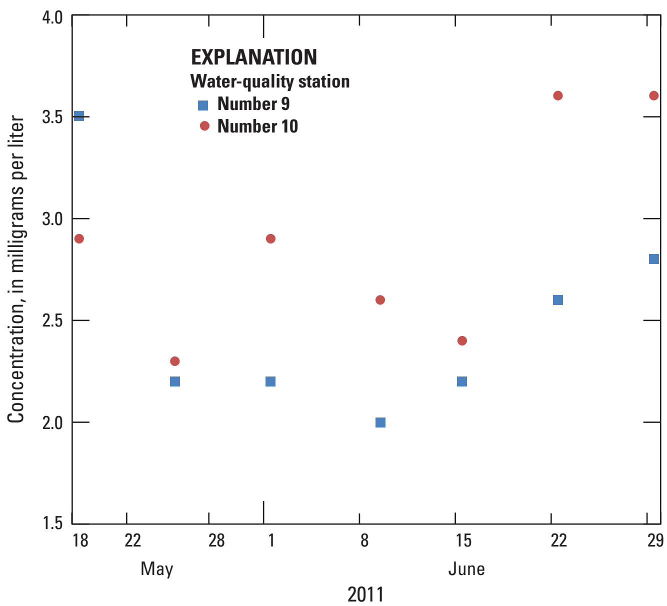

Figure 19. Concentrations of oil and gasoline upstream (water-quality station number 9) and downstream (water-quality station number 10) of the Morganza Floodway to the Atchafalaya River during the 2011 flood.

downstream ranged from 2.3 to 3.6 mg/L with a median concentration of 2.9 mg/L. These concentrations were within the range of oil and grease concentrations measured at station number 6 from 1974 through 1978 (0 to 9.6 mg/L with a median concentration of 0.63 mg/L; Saito and others, 2010). The first weekly sample (May 19, 2011) had oil and grease concentrations that were higher in water upstream than concentrations in water downstream from the Morganza Floodway (fig. 19). In the following six weekly samples, all concentrations of oil and grease were higher in the downstream samples than in the upstream samples (fig. 19). Higher concentrations downstream cannot necessarily be attributed to water from the floodway because oil and gasoline samples were not collected in the floodway during the 2011 flood.

Summary and Conclusions

High streamflow associated with the 2011 Mississippi River flood was predicted to result in record concentrations and fluxes of sediment, nutrients, and pesticides throughout the lower Mississippi-Atchafalaya River subbasin. There was concern that water flooding agricultural lands and water diverted through flood-control structures located in areas of agricultural and industrial land use would negatively affect water quality in the lower Mississippi River and the Atchafalaya River. Although concentrations of sediment, nutrients, and pesticides measured during the 2011 flood were similar to historical concentrations measured at the water-quality stations, time-series data indicated that surface water contained higher concentrations of suspended sediment and nutrients in March than the concentrations measured during the 2011 flood. The contribution of more streamflow from the Ohio River subbasin (a subbasin with less agricultural and more forested and urban land use than the upper Mississippi River subbasin) during the 2011 flood probably had a dilution effect. When combined with the lack of source material of constituents that were measured in higher concentrations prior to the flood (March 2011), the result was lower constituent concentrations during maximum streamflow.

The annual suspended-sediment flux in 2011 was within the lower range of historical fluxes from the lower Mississippi-Atchafalaya River subbasin into the Gulf of Mexico; 49 percent of the annual 2011 flux was delivered to the Gulf during the 2011 flood with the record streamflow. Overall, there was a loss in suspended-sediment flux within the subbasin during the 2011 flood. The losses occurred along the lower Mississippi River, particularly between the Old River Control Structure and St. Francisville, Louisiana, because of a loss in stream power. Conversely, suspended-sediment flux increased along the Atchafalaya River between all water-quality stations. Sand-sized particles in the Atchafalaya River were resuspended more readily during periods of high streamflow, resulting in a gain in suspended-sand flux through the two outlets of the Atchafalaya River into the Gulf of Mexico.

Annual fluxes of nitrate and total phosphorus in 2011 were within the upper range of historical fluxes entering the Gulf of Mexico from the lower Mississippi-Atchafalaya River subbasin. The 2011 flood contributed approximately 50 percent of the 2011 annual flux of nitrate and total phosphorus to the Gulf of Mexico. During the 2011 flood, the flux of both constituents was conservative within the lower Mississippi-Atchafalaya River subbasin. Early predictions estimated that the large nitrate flux would result in the largest zone of hypoxia ever measured in the Gulf of Mexico; however, the nitrate flux was not as high as was expected, and the resulting zone of hypoxia was the tenth largest on record.

Water samples collected from the lower Mississippi-Atchafalaya River subbasin during the 2011 flood were analyzed for 136 pesticides and pesticide degradates. Of the 136 compounds, 118 did not have detections above the method reporting level. The remaining 18 compounds that had detections above the method reporting level fell into three categories: (1) compounds that were frequently detected and showed a response in concentration to the flood, such as acetochlor, atrazine and its three degradates (deisopropylatrazine, deethylatrazine, and hydroxyatrazine), metolachlor, and simazine; (2) compounds that were detected in nearly every sample at each station but usually in very low concentrations, which included: prometon, 2,4–D, alachlor, diuron, 3–4-dichloroaniline, metribuzin, and prometryn (also included in this list, although detected only once in water from the upper Mississippi River and not detected in water from the Arkansas River); and (3) compounds that were infrequently detected, such as the fungicides *cis*-propiconazole, *trans*-propiconazole, and metalaxyl, and the herbicide trifluralin. Fluxes for the most frequently detected pesticides with the highest concentrations (atrazine, metolachlor, acetochlor, and simazine) were in the middle to low range of historical fluxes. This finding indicates that the 2011 flood, although of historic proportions as far as streamflow, did not carry a similarly historic amount of pesticides into the Gulf of Mexico.

Diverting water through the Morganza Floodway did not appear to have a large impact on water quality in the Atchafalaya River. Petroleum hydrocarbons were not detected at stations upstream and downstream from the outlet of the floodway into the Atchafalaya River, and detections of oil and grease were low and did not show a distinct pattern between the two stations. It appears that there was nitrate processing and phosphorus transformation as conditions in the floodway became reducing. Nitrate concentrations decreased during the period that the floodway was open, suggesting that denitrification was occurring. Orthophosphate concentrations increased during the period that the floodway was open, probably from the release of phosphorus bound to fine-grained soils in the floodway as conditions became anoxic. This finding suggests that diverting water through the floodway could have water-quality implications.

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