Occurrence of phosphorus in groundwater and surface water of northwestern Mississippi

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Previous localized studies of groundwater samples from the Mississippi River Valley alluvial (MRVA) aquifer have demonstrated that dissolved phosphorus concentrations in the aquifer are much higher than the national background concentration of 0.03 milligram per liter (mg/L) found in 400 shallow wells across the country. Forty-six wells screened in the MRVA aquifer in northwestern Mississippi were sampled from June to October 2010 to characterize the occurrence of phosphorus in the aquifer, as well as the factors that might contribute to high dissolved phosphorus concentrations in groundwater. Dissolved phosphorus concentrations ranged from 0.12 to 1.2 mg/L with a median concentration of 0.62 mg/L. The predominant subunit of the MRVA aquifer in northwestern Mississippi is the Holocene alluvium in which median dissolved phosphorus concentrations were higher than the Pleistocene valley trains deposits subunit. Highest phosphorus concentrations occurred in water from wells located along the Mississippi River. A general association between elevated phosphorus concentrations and dissolved iron concentrations suggests that reducing conditions that mobilize iron in the MRVA aquifer also might facilitate transport of phosphorus. Using baseflow separation to estimate the contribution of baseflow to total streamflow, the estimated contribution to the total phosphorus load associated with baseflow at the Tensas River at Tendal, LA, and at the Bogue Phalia near Leland, MS, was 23 percent and 8 percent, respectively. This analysis indicates that elevated concentrations of dissolved phosphorus in the MRVA aquifer could be a possible source of phosphorus to streams during baseflow conditions. However, the fate of phosphorus in groundwater discharge and irrigation return flow to streams is not well understood.

Key words: Ground water, irrigation, nutrients, water quality

Introduction

Concentrations of dissolved phosphorus (DP) in groundwater typically are low because phosphorus tends to sorb to soil and aquifer sediments and is not readily transported in groundwater (Holman et al. 2008). For example, the estimated background concentration of orthophosphate for more than 400 shallow wells across the country was 0.03 mg/L as phosphorus (Dubrovsky et al. 2010). The principal sources of phosphorus to groundwater systems include overlying soils, dissolution of minerals that contain phosphate in aquifer sediments, agricultural fertilizer, animal waste, and leaking septic systems or infiltration of wastewater (Fuhrer et al. 1999). However, Dubrovsky et al. (2010) noted that DP concentrations in groundwater showed no correlation to fertilizer and manure use in agricultural areas, and similarities to concentrations in deep groundwater suggest that natural geologic sources might have a greater influence on concentrations in groundwater than anthropogenic sources.

High phosphorus concentrations in groundwater collected from piezometers in the western Netherlands were generally associated with high ammonia, near neutral pH, and anoxic conditions (Griffioen 2006). High concentrations of iron and manganese can also be found in locations where similar groundwater chemistry exists. Because phosphorus tends to sorb to iron oxides, reducing conditions that promote the dissolution of iron oxides may also release bound phosphorus into groundwater and facilitate its transport.

Concentrations of phosphorus in groundwater can influence surface-water quality especially during periods of low rainfall when the majority of flow in the streams is baseflow or by irrigation return flow during the growing season. In the Albemarle-Pamlico drainage basin in North Carolina, high phosphorus concentrations in the stream were a result of discharge of groundwater with naturally high phosphorus concentrations (Dubrovsky et al. 2010), and concentrations in the stream decreased with increasing streamflow. The transport of phosphorus in groundwater to surface water likely is affected by geochemistry in the hyporheic/riparian zone, which retains and(or) releases phosphorus depending on environmental conditions, and whether the groundwater discharges to the stream at discrete points or as diffuse inflow (Holman et al. 2008). Also, phosphorus in groundwater applied as irrigation to agricultural fields could be retained on soil particles and later be exported to streams by sediment during high-flow events.

A previous study indicated that water quality in the Mississippi River Valley alluvial (MRVA) aquifer varies depending on local geology. Generally, the MRVA aquifer can be divided into two subunits based on environmental setting of deposition and age (Saucier 1994), Holocene alluvium and Pleistocene valley trains deposits. Twenty-five wells screened in alluvium and 29 wells screened in valley trains deposits located in Arkansas, Louisiana, Mississippi, Missouri, and Tennessee were sampled as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program in spring 1998 (Gonthier 2003). Results from this study indicate that the Holocene alluvium contained greater concentrations of dissolved solids, ammonia, dissolved organic carbon, DP, and fluoride than the Pleistocene valley trains deposits. Data also indicated that water in the Holocene alluvium was older and under more reducing conditions than water in the Pleistocene valley trains deposits. Welch et al. (2009) reported that water from wells screened in the MRVA aquifer subunits had higher DP concentrations when compared to other shallow wells less than 61 meters (m) in depth screened in the Mississippi Embayment-Texas Coastal uplands aquifer system. In fact, the Holocene alluvium subunit of the MRVA aquifer had the highest median concentration of DP of all shallow wells (less than 61 m in depth), which was attributed to strong reducing conditions because soil permeability was lower and soil clay content was higher than the other subunit (Welch et al. 2009). Nine MRVA aquifer wells were sampled during 2009 in Tunica County, MS, and concentrations of DP ranged from 0.7 to 1.3 mg/L (Shedd Landreth, Mississippi Department of Environmental Quality Office of Land and Water Resources, written commun., 2009).

Welch et al. (2009) also compared DP concentrations with streamflow quartiles at the Tensas River at Tendal, LA, and at the Bogue Phalia near Leland, MS, to determine if elevated DP concentrations in groundwater affect surface-water concentrations. Using streamflow quartiles, maximum DP concentrations in the Tensas River were observed during the lowest flows indicating that groundwater discharge is a possible source of phosphorus to the stream. Baseflow concentrations in samples from the Bogue Phalia were lower than in samples from the Tensas River, but the median concentration of about 0.04 mg/L during baseflow conditions and an overall range of concentrations between 0.05 and 0.3 mg/L indicated a potential for groundwater discharge to be a contributing source of DP to the stream. Coupe (2002) reported that total phosphorus (TP) yields from the Tensas River basin and the Bogue Phalia basin in 1996 to 1997 were 0.2 and 0.24 metric tons per square kilometer, respectively, which was unexpected because the availability of point source contributions was considered minimal, and phosphate fertilizer use in the area was less than that used in the Midwest where total phosphorus yields in streams were lower.

Although previous studies indicate that DP concentrations were high at sampled locations, no broad investigations have been conducted in the MRVA aquifer. In addition, elevated concentrations in the aquifer could be a source to streams and rivers in the study area, and ultimately to the Gulf of Mexico; thus, it is important to quantify the occurrence of phosphorus in the aquifer. During 2010, a study was conducted to investigate the mechanisms that facilitate the transport of DP in the MRVA aquifer in Mississippi, as well as, to quantify the contribution of groundwater DP to surface-water loads. This paper describes the results of the study in which groundwater chemistry was analyzed for samples collected from 42 active irrigation wells, 1 abandoned irrigation well, and 3 Mississippi Department of Environmental Quality Office of Land and Water Resources monitoring wells. In addition, the contribution of DP from groundwater to baseflow loading was quantified using a streamflow partitioning program for two sampling sites in the Mississippi Embayment.

Hydrogeology and Study Area Description

The MRVA aquifer underlies an area of approximately 18,000 square kilometers (km^2) and 19 counties in northwestern Mississippi. The aquifer is composed of Quaternary age clay, silt, sand, and gravel deposited by the Mississippi River and its tributaries (Arthur 1995). Average aquifer thickness is 43 m with coarse gravel at the base that fines upward into a layer of silts and clays which form an upper confining unit that ranges in thickness from less than 3 to 30 m thick (Arthur 1994). Transmissivity values derived from six aquifer tests conducted from 1954 to 1971 at wells screened in the MRVA aquifer ranged from 1,100 to 4,700 square meters per day (m^2/d), and hydraulic conductivity values ranged from 40 to 120 meters per day (m/d) (Slack and Darden 1991). The two subunits of the MRVA aquifer differ in that the Pleistocene valley trains deposits are coarser in grain size; have a thicker sand and gravel layer; and are overlain by a thinner clay and silt surficial unit than the Holocene alluvium (Autin et al. 1991; Saucier 1994).

Water-use data compiled in 2000 placed the MRVA aquifer as third largest in withdrawals of 66 large aquifers across the Nation (Maupin and Barber 2005). Approximately 0.04 cubic kilometer per day (km^3/d) is withdrawn, mainly for irrigation purposes (Maupin and Barber 2005). Regional groundwater flow in the MRVA aquifer prior to pumping for irrigation was toward the Mississippi River and southward; however, modern pumping has reversed flow away from the Mississippi River and toward interior areas in northwestern Mississippi (Renken 1998). Precipitation likely is the primary source of recharge, but other contributors could be streams, lakes, upward movement from underlying aquifers, downward seepage from irrigated lands, and lateral groundwater flow from the Bluff Hills which bound the aquifer on the east (Boswell et al. 1968). Krinitzsky and Wire (1964) stated that 5 percent of annual precipitation (approximately 6.6 centimeters (cm)) is recharged to the aquifer. A groundwater flow model by Arthur (2001) estimated that aerial recharge to the aquifer is 6.4 centimeters per year (cm/yr). A baseflow separation technique, used nationally to estimate values of natural groundwater recharge to the principal aquifers, indicated that 12.7 to 25.4 cm is the mean annual recharge to the MRVA aquifer (Reilly et al. 2008).

The Tensas River at Tendal, LA sampling site drains approximately 800 km^2, and the mean annual flow (1935-98) for the Tensas River at this site is 10 cubic meters per day (m^3/d). Land use in the basin is mostly agricultural (greater than 87 percent) with about 6.5 percent classified as forested wetland (Vogelmann et al. 1998). The Bogue Phalia surface-water sampling site drains approximately 1,250 km^2, and the mean annual flow from 1996 to 1997 was 18 m^3/s. Land use in the drainage area is predominantly agriculture with 71 percent of the land used for row crops and 15 percent in small grains such as wheat or rice.

Methods

In 2010, the U.S. Geological Survey (USGS), Mississippi Water Science Center, in cooperation with the U.S. Army Corps of Engineers, Vicksburg District, began collecting samples from groundwater in the lowlands part of the Yazoo River Basin in northwestern Mississippi, an area referred to locally as the "Delta". To assess the occurrence of phosphorus in the MRVA aquifer, water samples were collected and analyzed for a variety of chemical constituents from 46 wells previously described. The wells were each sampled one time from June to October 2010 for acid-neutralizing capacity (ANC), bicarbonate, calcium, silica, iron, manganese, arsenic, phosphorus, and field properties (pH, water temperature, specific conductance, turbidity, and at four wells, dissolved oxygen and depth to water).

Site Selection

Using a Geographic Information System (GIS) program, an equal-area grid of 50 cells was created across the entire area (figure 1). A center point was then generated for each study cell, which acted as the location for well selection within each cell. Well sampling sites were then chosen based on this location so that the sites remained equally-spaced across the Delta. The selected sites were limited to wells screened in the MRVA aquifer at depths ranging from 21.3 to 61 m below land surface (BLS).

Groundwater Sampling

One water sample was collected from 42 active irrigation wells, 1 abandoned irrigation well, and 3 Mississippi Department of Environmental Quality Office of Land and Water Resources monitoring wells from June to October 2010. Field measurements of pH, specific conductance (SC), and temperature were monitored using a multi-parameter probe with a flow-through cell. Turbidity was determined using a portable field turbidimeter. ANC was measured in the field using the inflection-point titration method as outlined by Rounds (2006). Samples collected from the three monitoring wells and the abandoned irrigation well were collected with a portable, submersible pump after purging several casing volumes and field measurements stabilized according to USGS protocols (Koterba et al. 1995). The high-capacity (greater than 3,800 liters per minute) irrigation wells were pumping when sampled, and were assumed to have had at least three well volumes purged before sample collection. All samples were shipped overnight on ice for analysis at the USGS National Water-Quality Laboratory (NWQL) in Denver, CO. Iron, manganese, and arsenic were quantified using inductively-coupled plasma methods, major ions were measured using atomic absorption spectrometry, and nutrient concentrations were quantified using colorimetry (Fishman and Friedman 1989).

The observation wells were 10 cm in diameter, and ranged in depth from 21 to 32 m BLS. Two of the observation wells had stainless steel casing, and one was cased with polyvinyl chloride (PVC). The abandoned irrigation well was 41 cm in diameter, cased with stainless steel, and was screened from 21 to 37 m BLS. The 42 active irrigation wells ranged in depth from 31 to 43 m BLS and were cased with stainless steel. Water samples were collected as near as practical to the wellhead, often at discharge outlets, from wells used to supply water for catfish ponds or for irrigating fields of rice, cotton, corn, and soybeans. The sampling points precluded collection of dissolved oxygen data at the 42 active irrigation wells. Site selection and sample collection was conducted in conjunction with personnel from the Mississippi Department of Environmental Quality Office of Land and Water Resources and the Yazoo Mississippi Delta Joint Water Management District.

Depth-interval sampling

In June 2008, as part of the NAWQA Agricultural Chemical Transport study, depth-interval sampling was conducted at five temporary sampling points at a site in Bolivar County, northwestern Mississippi. Water-quality samples and field property data for the temporary sampling points were collected using a peristaltic-type pump with Teflon®[1] tubing extended through the drill flights of the direct push equipment used to install the sampling points. Wells were purged and sampled following protocols outlined in the USGS National Field Manual (U.S. Geological Survey, variously dated). Field dissolved oxygen (DO) measurements, as well as temperature, pH, and SC, were made in a 50-milliliter (mL) cup attached to the multiparameter probe.

Baseflow analysis

Baseflow separation was used to estimate the contribution of groundwater discharge to streamflow at the Tensas River at Tendal, LA, and the Bogue Phalia near Leland, MS, two streams that were sampled as part of the NAWQA Program (Coupe 2002) from 1996 to 2000 and from 1995 to 2007, respectively. Using LOADEST (a FORTRAN-

[1]The use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Government.

based program developed by Runkel et al. 2004) and following procedures used by Rebich and Demcheck (2007), daily DP loads were calculated from measured DP concentrations in the samples and mean daily flow.

A streamflow partitioning program was used to estimate the contribution of groundwater discharge to baseflow, and subsequently the contribution to phosphorus loading in the streams. The baseflow index (BFI) program described by Wahl and Wahl (1988) uses a local minimums approach with a recession slope test to calculate the ratio of baseflow to total flow volume for a given year. For each daily flow value, a percentage estimate was made for the portion that could be attributed to baseflow. The percentage estimate of baseflow was multiplied by the DP load to estimate the portion of the DP load attributed to baseflow. This estimate of baseflow contribution assumes two things: (1) that TDP concentration in the stream remains constant and there are no contributions of flow from irrigation return flow, and (2) that the baseflow load model and the total flow model are the same.

Results and Discussion

Groundwater quality in the MRVA aquifer

Quality of water in the MRVA aquifer can be affected by overlying soil types, heterogeneity of aquifer sediments, aquifer chemistry, and the lack of a confining unit in some areas, which allows for infiltration of anthropogenic compounds such as fertilizers and pesticides (Welch et al. 2009; Gonthier 2003). Groundwater samples collected from June to October 2010 show variability in values for pH, specific conductance, bicarbonate, calcium, silica, iron, manganese, arsenic, and phosphorus in the 46 wells (table 1). Chemistry in the aquifer is likely affected by the presence or absence of dissolved oxygen (DO). As DO is consumed by organic compounds and microorganisms in an aquifer, oxidation-reduction (redox) conditions typically progress sequentially from an oxygen-reducing environment to nitrate-, manganese-, iron-, sulfate-reducing conditions, and finally methanogenic conditions under which organic carbon is reduced to form methane (Chapelle 2000). High dissolved iron and manganese concentrations that exist in the MRVA aquifer (table 1) indicate reducing conditions are occurring in the aquifer.

DP was detected in water from all 46 wells at concentrations ranging from 0.12 to 1.17 mg/L (table 1). In general, the highest concentrations occurred in wells located in counties bordering the Mississippi River (figure 1). As noted by Welch et al. (2009), higher DP concentrations were found in water from wells screened in the Holocene alluvium subunit of the MRVA aquifer (figure 2) than in wells completed in the Pleistocene valley trains deposits. The median concentration in the Holocene alluvium was 0.72 mg/L, which was twice the median concentration in the Pleistocene valley trains deposits, 0.36 mg/L. Because the only chemical constituent that differed between the two subunits in this dataset was DP, higher median concentrations in the Holocene alluvium might be attributed to the fact that the alluvium is finer-grained in particle size and also has a thicker clay confining unit than the Pleistocene valley trains deposits subunit. Because fine-grained particles have high phosphorus sorption capacities (Carlyle and Hill 2001), there might be more phosphorus available for desorption.

There are three possible sources for the phosphorus found in groundwater from the alluvial aquifer – anthropogenic sources such as fertilizers, a natural source in the soil or aquifer sediments, or a combination of both. Several factors suggest that the principal source of DP in the MRVA aquifer is likely a natural source. Although the Delta is used extensively for agriculture, application of phosphorus-based fertilizers in the area is usually less than 0.7 metric ton per square kilometer (Coupe 2002), and estimates of vertical recharge to the aquifer are low, ranging from 5.8 to 10.9 cm/yr (Green et al. 2009; Arthur 2001; Krinitzky and Wire 1964). Also, travel time through the unsaturated zone in an area where the confining unit is thin was estimated to be 16.8 years (Green et al. 2009). Welch et al. (2009) reported only a weak correlation between agricultural land use and the occurrence of DP in the Holocene alluvium. These factors suggest that anthropogenic activity is not the primary source of DP in the MRVA aquifer. High concentrations of DP were also reported in shallow Tertiary wells of the Mississippi Embayment-Texas Coastal uplands aquifer system which underlies the MRVA aquifer (Welch et al. 2009) but where land use is predominantly forested. The widespread occurrence of phosphorus in the two MRVA aquifer subunits, coupled with the occurrence of DP in groundwater from shallow Tertiary wells with differing land use, suggests that there is a geologic source for the DP.

Effect of reducing conditions on dissolved phosphorus concentrations

In oxygenated environments, concentrations of iron and manganese generally are less than 100 micrograms per liter (μg/L) because iron and manganese form oxide and oxyhydroxide complexes that are not soluble in oxidizing conditions (Deutsch 1997). However, as oxygen is consumed in an aquifer, concentrations of iron and manganese tend to increase with the dissolution of the complexes. Water from the 46 sampled wells contained concentrations of iron ranging from 3,100 to 21,400 μg/L with a median concentration of 6,900 μg/L and concentrations of manganese ranging from 180 to 1,700 μg/L with a median concentration of 470 μg/L (table 1). There is a general association between dissolved iron and elevated phosphorus concentrations that suggests that reducing conditions that mobilize iron also may facilitate transport of phosphorus (figure 3). It appears that above 10,000 μg/L of iron, there is a direct relation between increasing concentrations of DP and iron (figure 3). Carlyle and Hill (2001) note that the reduction of iron(III) to more soluble iron(II) in anaerobic conditions may play an important role in controlling DP concentrations because iron hydroxides that bind phosphorus are being reduced to the more soluble iron(II) form. A study conducted during June 2008 at a site in Bolivar County, MS, to investigate the movement of nitrate through the unsaturated zone showed that conditions in the aquifer become reducing at a depth of 4.4 m below the water table where nitrate is absent and iron concentrations are increasing. Samples collected from six vertical sampling points at the site in Bolivar County, MS, show a positive correlation ($p = 0.01$) between TP and increasing depth within the aquifer (figure 4). In addition, dissolved iron concentrations range from an estimated 6 to 17,000 μg/L with depth in the aquifer indicating increasingly reducing conditions. A possible mechanism for increasing TP concentrations with increasing dissolved iron is that iron (II) is more soluble than iron (III) causing a reduction in the number of oxyhydroxide sorption sites for TP.

It should be noted that arsenic was detected in water from all the MRVA aquifer wells, with concentrations ranging from 0.13 to 100 μg/L and a median concentration of 2.2 μg/L (table 1). Arsenic, which occurs naturally in rocks, soil, water, air, plants, animals, and is anthropogenically derived from arsenic-based pesticides, is often found in groundwater where DP and iron are in solution. The occurrence of arsenic in the MRVA aquifer appears to be loosely associated with the occurrence of DP (figure 5). In general, water from wells with phosphorus concentrations above 0.8 mg/L tends to have high arsenic concentrations. Arsenite, the dominant phase of arsenic in reducing conditions, adsorbs weakly to iron oxide surfaces, especially at pH values ranging from 6 to 9 (table 1; Hinkle and Polette 1999). Because of the similarity in the occurrence of iron, DP, and arsenic, reducing conditions are most likely increasing the dissolution of phosphorus and arsenic bound to iron oxide surfaces in the MRVA aquifer.

Contribution to baseflow – phosphorus loading

Watersheds in the Mississippi Delta have been identified as having some of the highest total phosphorus yields in the Mississippi River basin (Robertson and others 2009), but the contribution of groundwater from the MRVA aquifer to the DP yields has not been determined. The extent to which phosphorus concentrations in groundwater samples are maintained in transfers to surface water is uncertain (House 2003), however using groundwater contribution estimates to streamflow from BFI, the times at which groundwater contributes to the DP load at two streams located in northeastern Louisiana and the Mississippi Delta were estimated. The baseflow load of DP for the Tensas River at Tendal, LA, from 1996 to 2000, was 23 percent (figure 6). Estimated

DP load contribution from baseflow in the Bogue Phalia near Leland, MS, from 1995 to 2007, was 8 percent (figure 6). The contribution of baseflow to the DP load was higher in the Tensas River than in the Bogue Phalia, which is a result of higher concentrations in baseflow samples as well as a greater proportion of the total flow attributed to baseflow by both BFI in the Tensas River. Higher concentrations in baseflow at the Tensas River may be because the basin is incised in the Holocene alluvium subunit of the alluvial aquifer where elevated median DP concentrations have been reported. The Bogue Phalia is incised predominantly in the Pleistocene valley trains deposits, which typically has lower DP concentrations than the Holocene alluvium. BFI does not account for irrigation return flow to the streams during the irrigation season (usually May to August), but it is a useful tool for providing an estimate for groundwater as a source.

During much of the year, the DP contribution to the total phosphorus concentration is small at both sites, on the order of 20 percent of the total concentration (figure 7). However, during low-flow periods, the DP can comprise as much as 50 percent (median) of the total phosphorus concentration in the Tensas River and as much as 70 percent (median) in the Bogue Phalia (figure 7). In the Tensas River, the highest percentage of total phosphorus that is dissolved occurs during the months of July through October (figure 7a). Lowest monthly mean discharge values for the Tensas River also occur during these months which would indicate that when groundwater makes up most of the streamflow, DP accounts for most of the in-stream total phosphorus (figure 7a). A similar relation between monthly mean discharge and percentage of DP exists for the Bogue Phalia (figure 7b), but the Bogue Phalia seems to have slightly higher percentage of DP in August and September compared to the Tensas River. September is the month in which the majority of the total phosphorus in the Bogue Phalia is composed of DP (median is about 65 percent), which also coincides with times of low flow indicating groundwater discharge to the stream. However, DP percentages are also high in August at a time when monthly mean discharge is twice the monthly mean discharge in September. A possible contributor of the high percentage of DP during August could be irrigation return flow.

Conclusions

DP concentrations in water from the MRVA aquifer ranged from 0.12 to 1.17 mg/L. The Holocene alluvium subunit of the MRVA aquifer had higher DP concentrations than water in the Pleistocene valley trains deposits. DP concentrations were loosely correlated to iron concentrations, and to a lesser degree, arsenic concentrations, in that increases in DP coincided with similar increases in these other constituents. Such results imply reducing conditions in the MRVA aquifer cause DP, arsenic, and iron to become more mobile. The lack of a large amount of phosphorus fertilizer application, high phosphorus concentrations in shallow Tertiary wells screened in geologic units underlying the MRVA aquifer where the land use is predominantly forested, and slow vertical movement through the unsaturated zone into the aquifer seem to indicate a geologic source for the phosphorus found in the aquifer.

Baseflow separation methods indicate that groundwater is a contributor to DP loads at the Tensas River at Tendal, LA, and the Bogue Phalia near Leland, MS. Higher load contributions were found in the Tensas River than in the Bogue Phalia, which corresponds to differences in the underlying geologic units with the Holocene alluvium having higher DP concentrations. In addition, the highest percentage of DP contributing to total phosphorus concentrations occurred at low flow, indicating that groundwater is the primary source of phosphorus during these periods. Additional study is needed to determine the extent to which phosphorus in groundwater is transported to surface water either by irrigation return flow or with groundwater discharge.

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Table 1. Summary of selected chemical constituent concentrations in samples from wells screened in the Mississippi River Valley alluvial aquifer, June to October 2010. [µS/cm, microsiemens per centimeter; mg/L, milligrams per liter, milligrams per liter; µg/L, micrograms per liter]

Constituent	**Minimum concentration**	**Median concentration**	**Maximum concentration**
pH	6.2	6.7	7.3
Specific conductance, in µS/cm, at 25˚C	296	590	1,600
Bicarbonate, in mg/L	160	370	620
Phosphorus, in mg/L	0.12	0.62	1.17
Silica, in mg/L	29.8	35.0	44.4
Calcium, in mg/L	29.9	81.0	200
Iron, in µg/L	3,100	6,900	21,000
Manganese, in µg/L	180	470	1,700
Arsenic, in µg/L	0.13	2.2	100

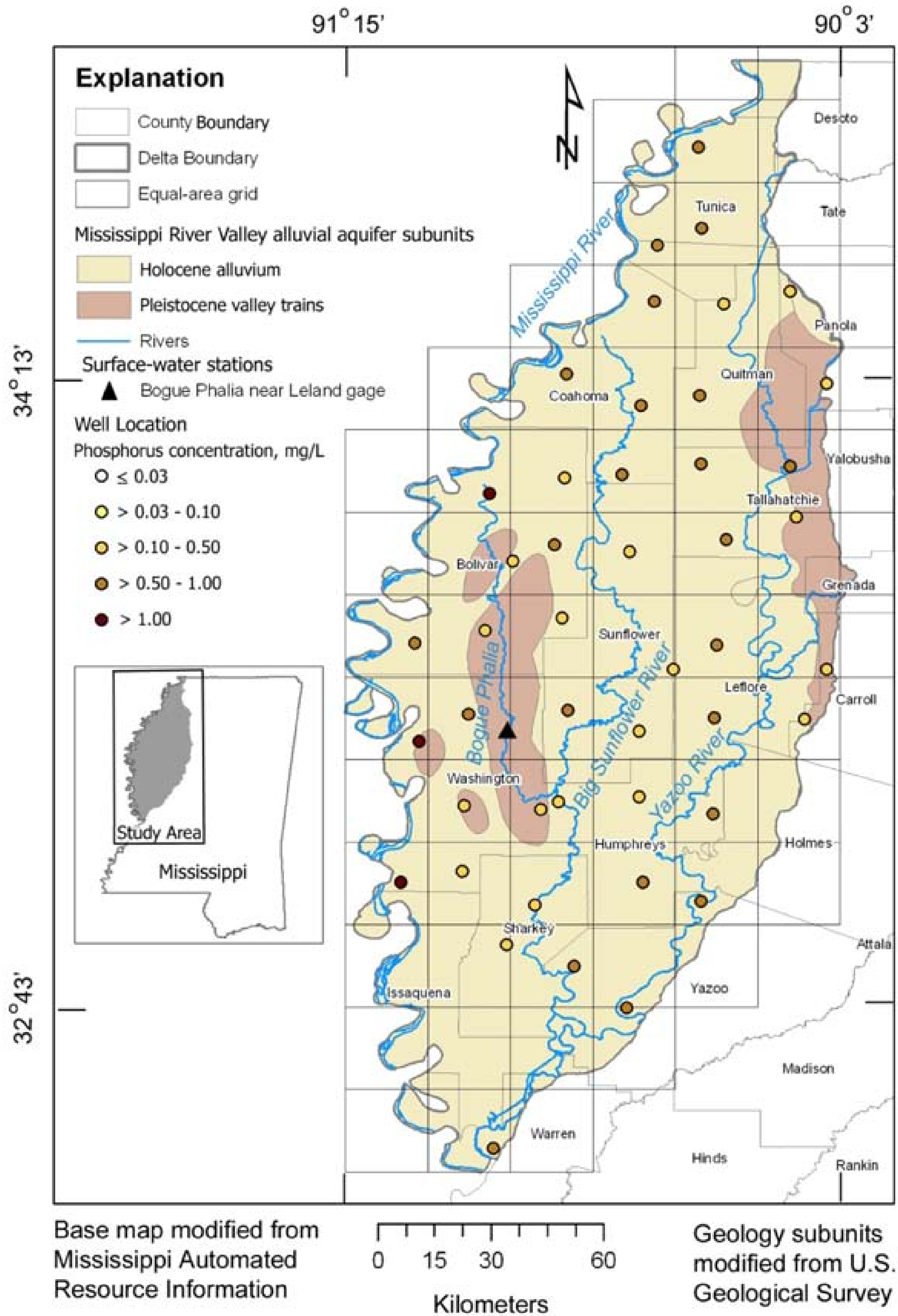

Figure 1. Map showing the equal-area grid for site selection and phosphorus concentrations at the sampled wells in northwestern Mississippi.

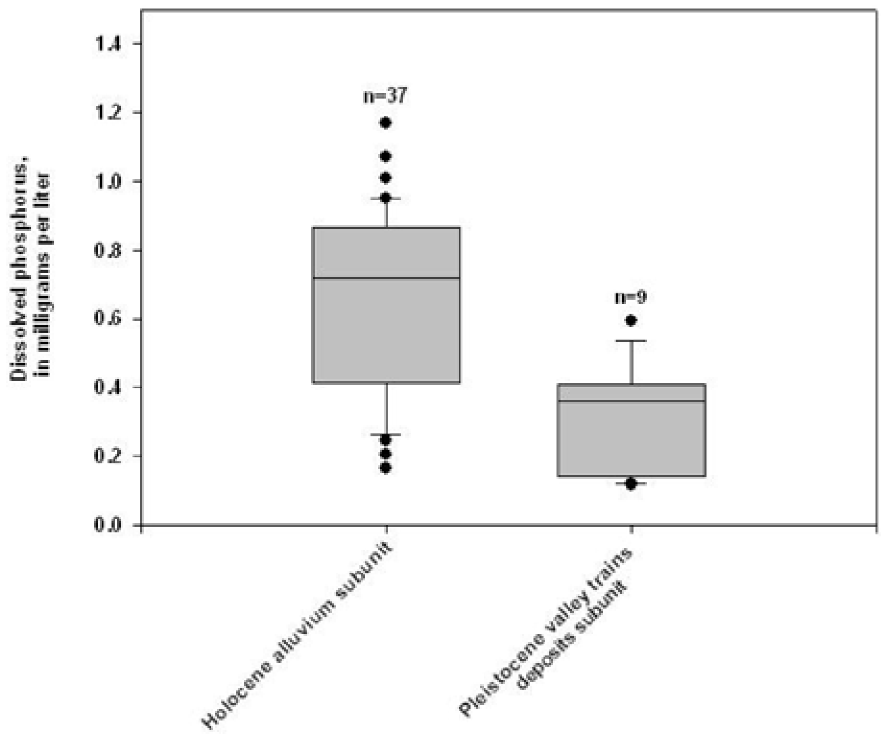

Figure 2. Concentrations of dissolved phosphorus in the two subunits of the Mississippi River Valley alluvial aquifer.

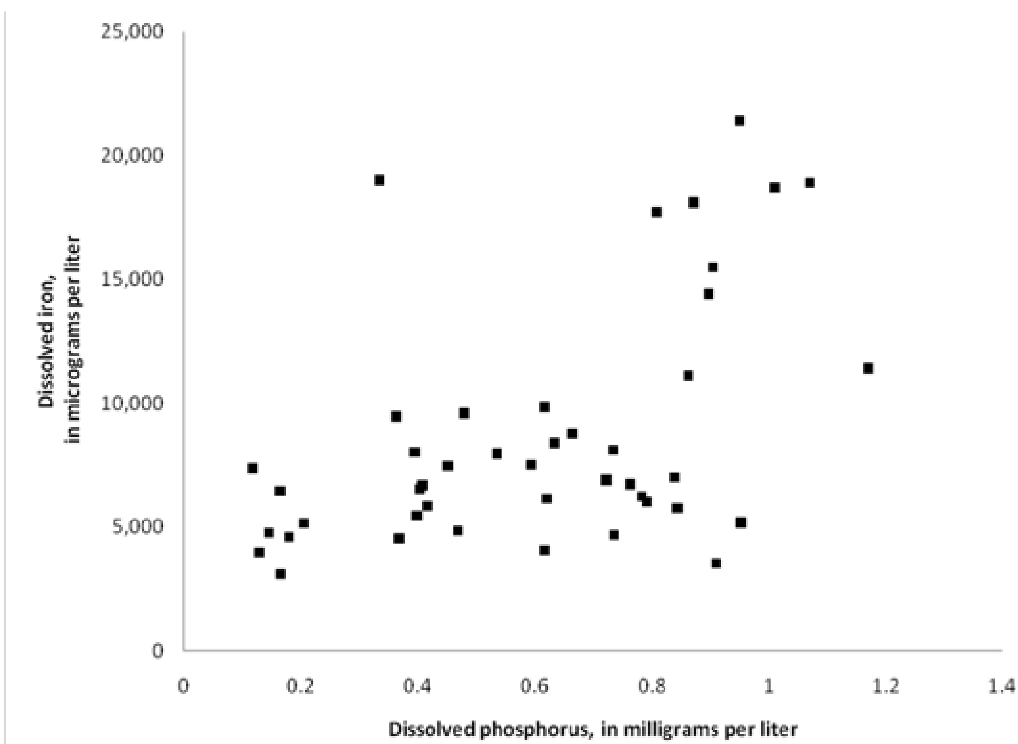

Figure 3. Relation between dissolved phosphorus and dissolved iron concentrations in water samples from the Mississippi River Valley alluvial aquifer, northwestern Mississippi.

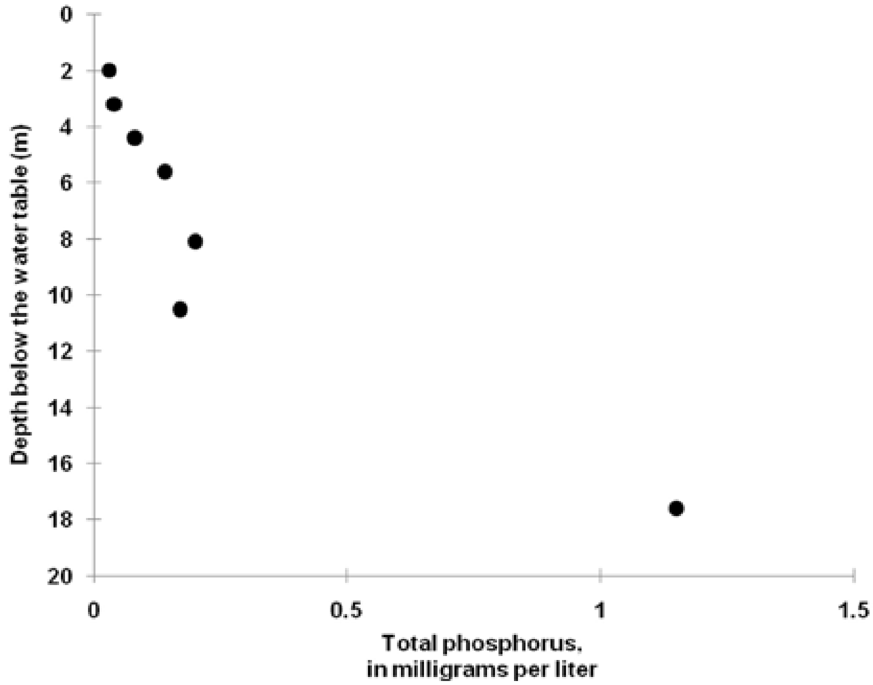

Figure 4. Relation between total phosphorus and depth below land surface in water samples from the Mississippi River Valley alluvial aquifer at a depth-interval sampling site in Bolivar County, northwestern Mississippi.

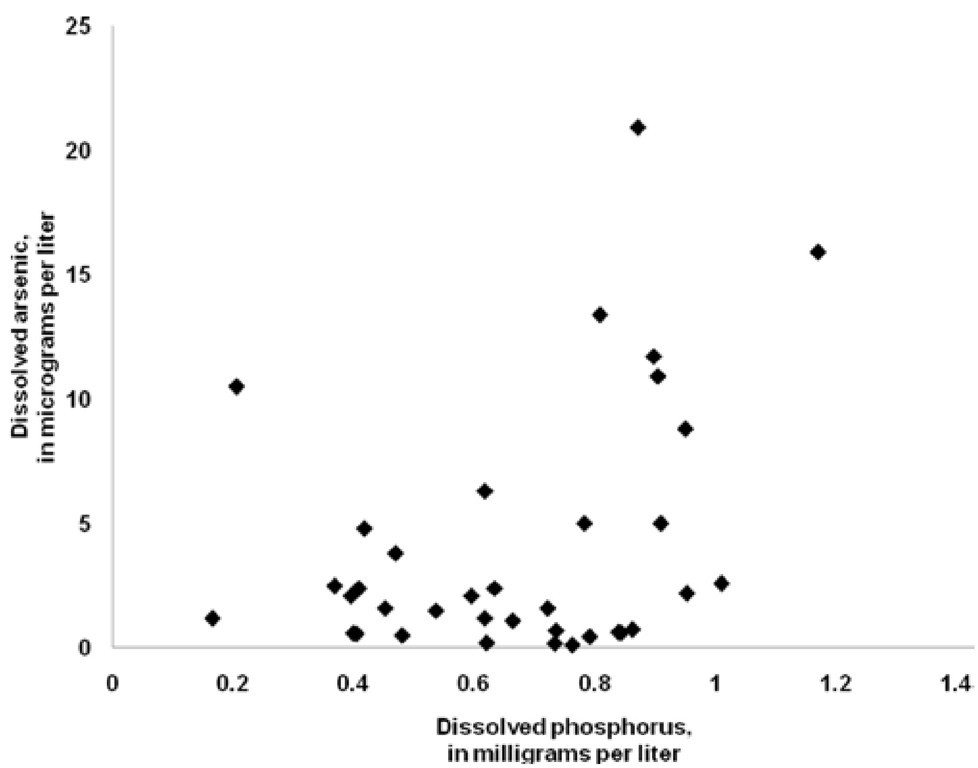

Figure 5. Relation between dissolved arsenic and dissolved phosphorus in water samples from the Mississippi River Valley alluvial aquifer, northwestern Mississippi. One sample with an arsenic concentration of 100 μg/L was not included in this plot for scaling purposes.

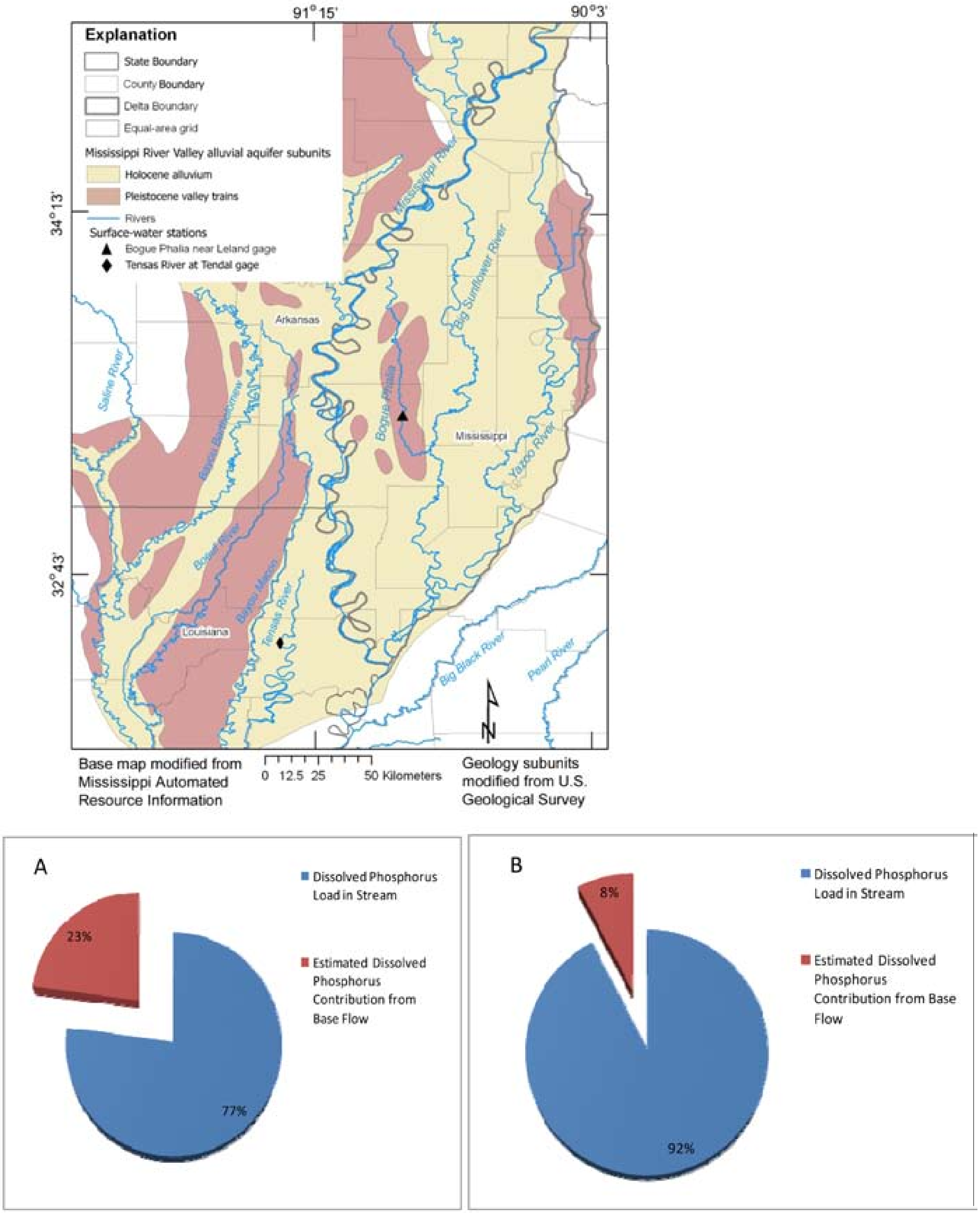

Figure 6. Estimated contribution of baseflow to the dissolved phosphorus load in (A) the Tensas River at Tendal, LA from October 1996 to September 2000, and (B) the Bogue Phalia near Leland, MS from October 1995 to October 2007. Inset map shows the location of the two surface-water sites.

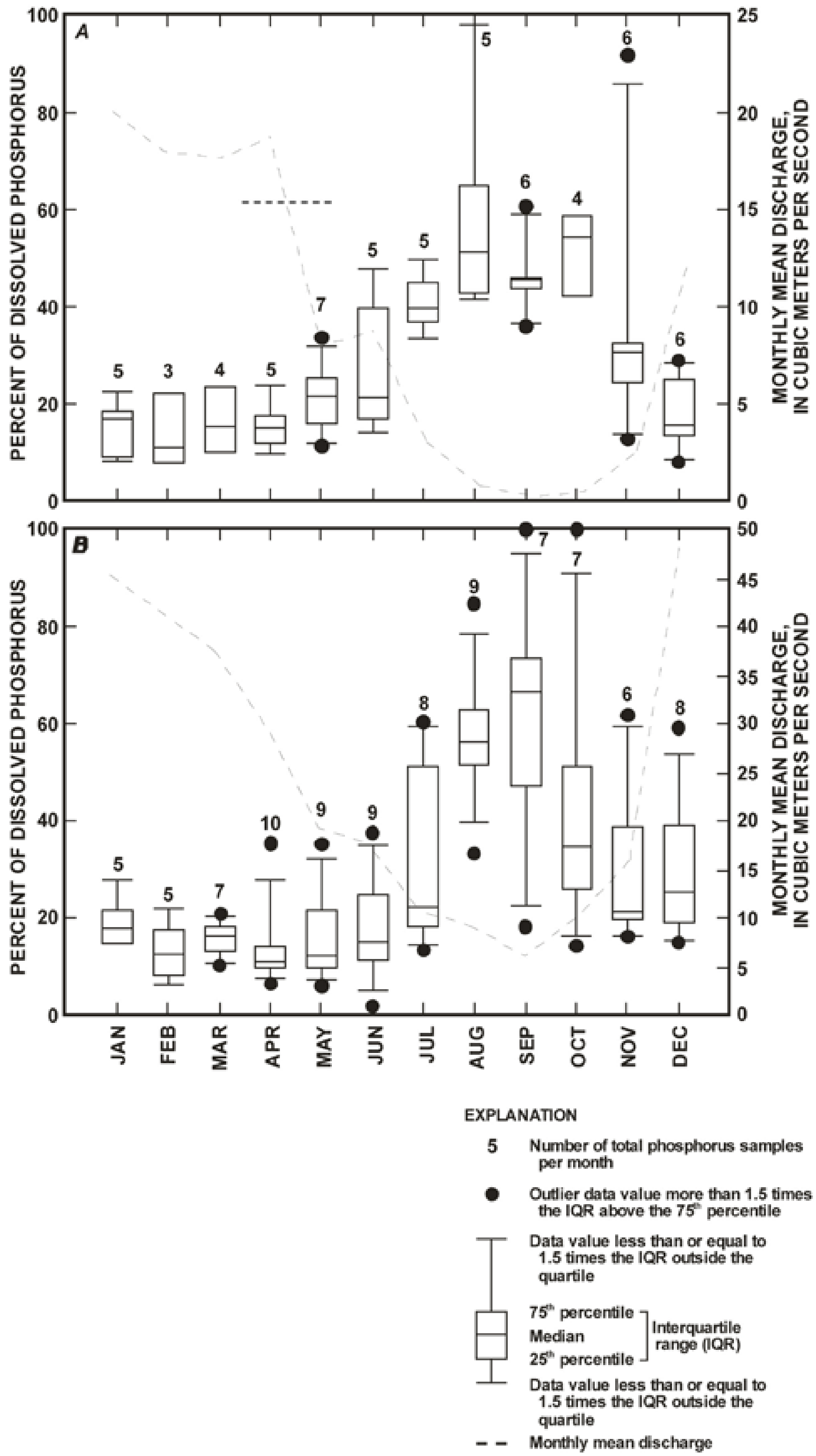

Figure 7. Percentage of dissolved phosphorus in the stream compared to monthly mean discharge from point samples taken at (A) the Tensas River at Tendal, LA, 1995 to 2000, and (B) the Bogue Phalia near Leland, MS, 1996 to 2001.