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# Nutrient Transport in the Yazoo River Basin, Mississippi

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## Introduction

This report seeks to summarize available information regarding the input, storage, processing and movement of nitrogen (N) and phosphorus (P) in the Yazoo River basin of northwestern Mississippi. Both published information and databases were examined. This document serves as a companion to the report by Simon et al. (in Preparation) on sediment transport in the Yazoo Basin. This introduction is intended to place these topics in a global context of problems associated with nutrients in aquatic ecosystems. The following section provides a description of the Yazoo River basin, and is followed by sections dealing with nutrient inputs such as fertilizer, point sources, and atmospheric deposition. Next, literature describing movement of nutrients from land to water and transport through the basin to the Gulf of Mexico is briefly summarized. Key nutrient sinks in the basin are identified and rough estimates of the total yields of N and P from the Yazoo basin to the Mississippi River are presented and compared to estimates published by others. Finally, Yazoo basin stream nutrient concentrations recorded in databases maintained by the USGS, the US EPA and this laboratory were used for spatial and temporal analyses. Spatial analyses consist mainly of contrasts between the two main geographic regions within the Yazoo River basin and on the effects of watershed size. Temporal analyses examine seasonality of nutrient levels.

Ecosystems require regular nutrient inputs to function properly. Among these are carbon, nitrogen, phosphorus, potassium, iron, selenium and silicon. Through photosynthesis, plants convert inorganic materials containing these elements into organic compounds, which are then passed through food webs to other life forms. In aquatic ecosystems, phytoplankton cells typically contain N and P in a ratio ranging from 5 to 20, depending on species characteristics. N exists in many forms in aquatic ecosystems: as dissolved gas, ammonia and ammonium ( $\text{NH}_3$  and  $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ) and organic forms that may be either particulate or dissolved. In enriched systems, nitrate, which is highly mobile, is often the dominant form of N. Because they must be converted into different forms to be available to plants, particulate and organic forms have less short term impact than the readily available ammonia ions, nitrites and nitrates. Unlike P, inorganic N does not sorb strongly and can be transported in both particulate and dissolved phases in surface runoff, in the unsaturated zone of soil, and in groundwater (FISRWG 1998). Atmospheric cycling of N is also significant. For example, an average of about 40% of the inorganic N applied as fertilizer cycles through the atmosphere and is redeposited.

Although any nutrient is important, productivity cycles in disturbed systems are generally dominated by anthropogenic inputs of N and P (Carpenter et al. 1998). For example,  $\text{NO}_3^-$  loads in 35 of the largest rivers in the world were highly correlated ( $r^2 > 0.8$ ) with point and nonpoint source N loads (Caraco and Cole 1999). Human impacts on the global N cycle are significant, primarily due to the use of synthetic fertilizer, which accounts for more than half of the human alteration of the N cycle. Overall, human fixation of atmospheric N during fertilizer manufacture, combustion of fossil fuel, and production of legumes increased globally by a factor of 2 to 3 between 1960 and 1990, thus contributing significantly to nonpoint source flows of N (Howarth et al. 2002, Committee 2000). Agricultural sources contribute more than 70% of the N and P delivered to the Gulf of Mexico by the Mississippi and Atchafalaya Rivers (Alexander et

al. 2008). Corn and soybean cultivation is the largest contributor of N (52%), followed by atmospheric deposition (16%), while P originates primarily from animal manure (37%) and then from corn and soybeans (25%).

N and P are major limiting nutrients for plant growth in aquatic systems with sufficiently low water turbidity and velocity. Although there are exceptions, P inputs normally control eutrophication in freshwater systems while N inputs govern marine systems (Howarth et al. 2000). Lakes, rivers, wetlands and coastal waters with elevated levels of N and P experience excessive plant growth which results in dissolved oxygen depletion, high levels of turbidity, fish kills and other problems.

Because of the detrimental results of over enrichment, nutrient transport from the continental United States into coastal waters is of great concern. Between 1960 and 2000 the flux of N from the Mississippi River into the Gulf of Mexico has tripled and P has doubled, creating a seasonal hypoxic zone spread over several thousand square miles (Rabalais et al. 1999). The Yazoo River Basin which supports intensive crop cultivation is a significant tributary to the Lower Mississippi River, and the proximity of the basin to the Lower Mississippi means that relatively high percentages of the Yazoo N and P loads are delivered to the Gulf (Alexander et al. 2008).

## Basin description

The Yazoo River Basin is the largest river basin in Mississippi and encompasses nearly 34,600 km<sup>2</sup>. Within the drainage, there are approximately 39,515 km of rivers and streams (Guedon and Thomas 2004). The basin comprises 30% of the land area of the state and is home to one-fifth of the population (Yazoo River Basin Team 2006). The Yazoo River proper is formed by the confluence of the Tallahatchie and Yalobusha Rivers in the central portion of the basin near Greenwood, Mississippi. The Yazoo then flows southwesterly for 315 km to join with the Mississippi River near Vicksburg. The Yazoo Basin is separated into two distinct topographic regions, the Bluff Hills (Hills) to the northeast, and the Mississippi Alluvial Plain (Delta) to the southwest, although the regions remain adjacent for the length of the basin (Figure 1). Land use is predominately agricultural, with agricultural uses comprising 60% of the area of the sparsely populated basin (Runner et al. 2002, USGS 1990, Guedon and Thomas 2004) (Figure 2). The majority of agricultural use is in the Delta, while the Hills support a variety of land uses with much smaller areas of cultivation.

### *Hills*

The Hills occupy about 16,600 km<sup>2</sup> or about half of the basin. This region supports a complex mosaic of pine and oak/hickory forests, pastures, and small farms. Relatively flat cultivated floodplains flank most stream channels, with steep forested or grassed hillslopes rising to the watershed divides. Hill soils (primarily loess and loess-derived alluvium) are highly erodible, and channels are extremely unstable, producing average annual sediment yield about twice the national average (~ 1000 t km<sup>-2</sup>) for watersheds of this size (Shields et al. 1995a). Streams in the Hills tend to be channelized and thus have straight and wide channel beds composed of either sand, sand and gravel, or cohesive clay, and steep, high banks prone to failure. Except during higher flows, water depths are shallow (Shields et al. 1994). Due to their inclusion in federally-funded erosion control programs (e.g., Hudson 1997), the geomorphology of Hill watersheds has been described in several publications (e.g. Whitten and Patrick 1981, Little et al. 1982, Simon and Darby 2002).

European settlement (1835-1850) of the Hills was accompanied by deforestation and cultivation of hillsides that produced rapid erosion and gully development, and up to 2 m depth of valley sedimentation. To capture sediment and control Delta flooding, flood control reservoirs were constructed on the Coldwater (Arkabutla Lake), Tallahatchie (Sardis Lake), Yocona (Enid Lake), Yalobusha (Grenada Lake) Rivers from 1940 thru 1954. These reservoirs are located along the boundary between the Hills and the Delta and control runoff from about two-thirds of the Hills region (Figure 3). In order to drain valley bottoms for agriculture, nearly all perennial channels were channelized at least once between ca. 1880 and 1965. Fluvial response between about 1965 and the present is consistent with conceptual models of incised channel evolution (Schumm et al. 1984, Simon 1989a, Simon and Thomas 2002): channels responded to channelization and reservoirs by incising as much as 5 m between about 1960 and the present (Whitten and Patrick 1981, Grissinger et al. 1982). A network of small

watershed reservoirs was constructed in the 1960s, and extensive channel and watershed erosion control works were constructed throughout the Hill tributary watersheds, mostly between 1986 and 1996.

### *Delta*

The Delta comprises a slightly larger area than the hills, or about 18,000 km<sup>2</sup>. In contrast to the Hills, the Delta is predominately flat farmland with an average gradient of 0.19 m/km. Agriculture in the Delta developed later than in the Hills. During the 1920s and 1930s the Delta experienced a significant decline in human population primarily because of agricultural mechanization. Major crops of the Delta include soybeans, cotton, corn, rice, grain sorghum and catfish. About two-thirds of the Delta is cultivated for row crops and about two-third of row cropland is irrigated.

Soils in this region consist of clay and fine sand from alluvial deposition of the ancestral Mississippi and Ohio Rivers (Guedon and Thomas 2004). Bottomland soils are often heavy clay (“gumbo” or “buckshot”), but may be sandy silts, while occasionally low sandy ridges occur in ridge and swale topography. However, much of the productive land has been laser-leveled and is drained by a network of ditches, transforming the complex of wetlands, rivers, sloughs and bottomland hardwood forest into a highly productive agricultural region. Prior to laser-leveling, the soils and topography of the Delta reflected alluvial activity, principally the overflow of the Mississippi River. However, completion of main-line levees along the River and construction of a system of levees, bypass channels and reservoirs along Yazoo River tributaries has greatly reduced the frequency, extent and duration of flooding in the Delta. There are also numerous oxbow lakes throughout the Delta. Due to the presence of natural lakes and catfish ponds, surface water comprises 3% of the Delta landscape. Streams in the Delta are typically sluggish due to the limited slope, and are periodically turbid from sediment runoff. Bottom material varies from clay to fine sand. Most river and stream channels have been straightened to facilitate drainage.

### *Indicators of environmental quality*

Water quality assessments have been conducted for 2,600 km (~18%) of the 15,000 km of perennial stream channels in the basin by Mississippi Department of Environmental Quality (MDEQ). These efforts have been focused on the Hills using the Environmental Protection Agency Integrated Reporting category system, and 74% of the assessed streams that have been found to be impaired (Guedon and Thomas 2004). Future studies will be conducted to determine the sources of impairment. Causes of impairment already noted include biological (50% of impaired stream miles), pathogens, DDT/ toxaphene, organic enrichment/low dissolved oxygen, PCB's, salinity, and mercury. Indicators of environmental quality are currently being produced through indices of biotic integrity for the Delta (Guedon and Thomas 2004). Initial research failed to establish a link between physical habitat quality and biotic integrity (Shields et al. 1995b).

The Mississippi 2006 Clean Water Act section 303(d) list of impaired waterbodies, as reported by the MDEQ, does not include any waterbodies that are impaired due to nutrients for which monitoring data exist. Twelve TMDLs have been

completed for Delta waterbodies that are considered to be impaired due to nutrients (Table 1). The 303(d) list does, however, contain 79 waterbodies in the Yazoo basin that have been listed for potential impairment due to nutrients. Under a consent decree, the MDEQ had to propose TMDLs for all of these waterbodies by December 31, 2007 unless monitoring data became available for their delisting. Many of these waterbodies are located within the Delta. Because the distinctive nature of the Delta, no adequate method of quantifying changes in aquatic system biotic integrity and function has been identified. However, a fish-based index of biotic integrity currently under development holds promise for accurately identifying waterbody impairment from pollutants, including nutrients.

Within the Hill regions of the Yazoo River Basin, the MDEQ has collected nutrient data in association with sites used to develop an invertebrate index of biotic integrity (IBI) for use in bioassessment of waterbodies throughout most of the state, excluding the Delta region. Use of this IBI has resulted in removal of nutrients as the cause of impairment for six waterbodies within the Hill region of the Yazoo River Basin. As a part of this IBI project, 133 streams were sampled for nutrient concentrations in the non-Delta regions of Mississippi (Appendix). Additionally, surface water in 50 large (>200 ha surface area) and 46 small (<200 ha surface area) lakes and reservoirs throughout the state were sampled periodically in a recent study of lake water quality, including nutrient concentrations.

The Yazoo River Basin has two federal threatened and four federal endangered species. This basin also includes two Hill-region streams, Coldwater River and Tippah River, proposed for review as potential Mississippi Natural and Scenic Waterways System water bodies.

## Nutrient inputs to basin

Nutrients enter wetlands, streams, and lakes in the Yazoo River Basin from the atmosphere, point source discharges, and in runoff. Dissolved N also enters surface waters in groundwater. Nutrients in runoff and groundwater are derived from soils, legumes, atmospheric deposition, human or animal wastes and fertilizer. Agriculture is the dominant source of N and P discharges to surface waters in the U. S. Soil N mineralization and fertilizer N applications are the greatest sources of inorganic N in the Mississippi River basin (Figure 4).

In 2006, as a partial result of the USGS National Water-Quality Assessment, a county-level nutrient input report and data base were published for the conterminous United States (Ruddy et al. 2006). The data base contains estimated inputs of N and P from fertilizer (farm and non-farm), manure from farm animals (confined and unconfined), and atmospheric deposition for each county of the U.S for the period 1981-2001, a period of rather stable overall fertilizer loading (Figure 4). The sources for the data are given in Table 2, and loadings were derived as follows:

Fertilizer – Data were converted from tons of fertilizer to kilograms of N and P based on chemical composition of each product. Guidelines were set to identify and disregard questionable data, such as specified P compositions greater than 75 percent. County-level nutrient inputs were calculated by multiplying the state N or P input by the ratio of expenditures from county and state as described by Battaglin and Goolsby (1995). Non-farm fertilizer sales, if not available, were calculated based upon population density.

Manure – Methods were those described by Goolsby et. al (1999) to estimate nutrient content in the manure from various livestock. Differences in life cycles of farm animals throughout the year and nutrient losses in storage, handling, and application of manure were taken into account. Livestock population data were obtained from the Census of Agriculture that is released every five years; therefore a continuous record was not available. Error due to census regulations hindering the disclosure of a small percentage of livestock was noted.

Atmospheric Deposition – Nutrient inputs from atmospheric deposition were obtained from the NADP web page (<http://nadp.sws.uiuc.edu/>). Using point location data and GIS inverse distance-weighted interpolation, a grid was formed using a cell size of 1 km. Annual deposition rates for each county were then calculated by averaging the grids that fell within the county boundaries. The deposition rates were then multiplied by county area to obtain N mass.

In order to apply findings of Ruddy et al. (2006) to the Yazoo Basin, counties within the Basin were classified as being Delta, Hills, or both (Table 3). Averages and standard deviations were computed for Yazoo basin counties for 1981-2001. These statistics represent N and P inputs to the basin exclusive of crop N fixation, point sources and soil erosion. Results are summarized for each county in Table 3 and for the basin in Table 4, which shows that the average estimated N and P inputs to the Yazoo

Basin from fertilizer, manure and atmospheric deposition are about 124,000 and 16,000 metric tonnes, respectively. About 77% of all estimated N input and 86% of all estimated P input are in the form of fertilizer applied to farms, with an additional 10% and 23% of the N and P, respectively, from livestock manure (Figures 5 and 6 and Table 5). Non-farm fertilizer input comprised less than 1% of the nutrient loadings (Table 5).

The Delta receives a higher nutrient loading than the hills due to fertilizer applications to row crops. About 56% of both N and P inputs to the basin were from fertilizer applied to Delta farms while about 20% of inputs were due to manure input to Hill counties (Table 5). The top five basin counties for total N input were the Delta counties of Bolivar, Yazoo, Washington, Sunflower, and Tallahatchie. The top five counties for P input were Yazoo, Bolivar, Washington, Tallahatchie, and Sunflower, also all Delta counties. The findings of P fertilizer inputs to Delta counties are questionable since others report little or no application of P fertilizers due to the high P content of Delta soils (Snipes et al. 2004, Dabney et al. 2004). However, assuming 56% of the annual P input is in the form of fertilizer placed on Delta farmland (Table 5), and further assuming that the Delta is comprised of 18,000 km<sup>2</sup> of which 64% is in row crops, the mean annual P loading to Delta cropland is a modest 7.6 kg ha<sup>-1</sup>, which is not unreasonable.

Yazoo basin-wide mean annual N and P loading rates, based on figures in table 4 average 33.9 kg ha<sup>-1</sup> and 4.3 kg ha<sup>-1</sup>, respectively. Although nationally, most streams that drain areas with greater than 22.4 kg ha<sup>-1</sup> mean annual N loading have average N concentrations greater than 2.9 mg L<sup>-1</sup>. However, concentrations in the Yazoo tend to be lower, perhaps because of a warmer, wetter climate that that increases microbial activity in the winter and due other the increased uptake of N by plants during the longer growing season (Kleiss et al. 2000).

## Nutrient flux from land to water

Information on nutrient flux from land to water is available from long-term studies of runoff quality from fields and small plots, but not larger areas. These studies highlight the unsteady nature of nutrient flux from cultivated lands. Often the yield from a single storm can be nearly equal to the annual average (Schreiber et al. 2001). Most of the N and P leaving experimental fields and erosion plots is associated with eroded sediment. N and P flux from croplands is greatest during spring following fertilizer application and is highly unsteady, with much of the annual load occurring in a few storm events.

### *Hills*

McDowell and McGregor (1984) presented three years of observations of N and P flux from standard erosion plots (0.01 ha, 5% slope) in the Hills. Plots were cultivated for corn using 5 cultural systems including conventional tillage, reduced tillage and no till. Soils were fertilized with N (~17.0 tonne km<sup>-2</sup>) and P (~3.0 tonne km<sup>-2</sup>). Average yields for total N varied from 1.04 for tonne km<sup>-2</sup> (no-till) to 4.78 tonne km<sup>-2</sup> (conventional tillage). Average yields for total P varied from 0.2 for tonne km<sup>-2</sup> (no-till) to 1.75 tonne km<sup>-2</sup> (conventional tillage). About 90% of N and P flux from conventionally-tilled fields was transported in association with sediments rather than in solution. Similar studies at the same experimental farm using soybeans were reported by McDowell and McGregor (1980). In 1973, which was a very wet year, total losses of N and P from no-till soybeans were about one-tenth and one-sixth, respectively, of that from conventional tillage which was about 4.6 tonne km<sup>-2</sup> (N) and 1.8 tonne km<sup>-2</sup> (P). Most N and P flux from conventionally-tilled plots were transported by sediments, but solution P concentrations were greater from no-till plots. Most N and P movement occurred during the first few storms after fertilizer applications.

Schreiber et al. (2001) summarized four water years of observations from an experimental farm in the Hills and five years of data from five study watersheds in the Hills that were reforested by planting pines in 1939 (Figure 7). N yields from the conventionally-tilled lands were roughly half as great as for the Delta, but P yields were about twice as great as for the Delta. Yields from no-till fields were much lower than for conventional tillage, and yields from the forested watersheds were lower still, generally less than 5% of values for the conventionally-tilled hill lands.

### *Delta*

McDowell et al. (1989) presented results of a six-year study of N and P yields from silty soils used for growing cotton in the Delta. Runoff from gently sloping (0.2%) land fertilized with N but not P produced yields as shown in Table 6. Only about 18% and 8% of the N and P were transported in solution, the rest was associated with sediments. Both N and P yields were correlated with runoff water volume. Nitrate N concentrations were usually highest in the spring immediately after fertilizer applications. Average soluble N yield from one watershed was equivalent to about 4.5% of the annual fertilizer application. Soluble P exceeded the then-current USEPA water quality criteria (0.05 mg L<sup>-1</sup>) in about 97% of the runoff analyzed. Concentrations

of P greater than 0.2 mg L<sup>-1</sup> occurred mainly during September through January and were attributed in part to release from senescent plants and crop residues.

Additional findings were reported by Schreiber et al. (2001) for a 5.7-ha Delta field conventionally tilled for cotton and soybeans and monitored for three water years (Figure 7). P yields are not directly comparable to work by McDowell et al. (1989) due to different analytical procedures, but mean annual yields of N associated with sediment were 2.35 tonne km<sup>-2</sup>, similar to the level of 3.46 tonne km<sup>-2</sup> found by McDowell et al. (1989). Soluble N yields were about 37% of total yield, and soluble orthophosphorus was about 13% of the sediment-associated P. Schreiber et al. (2001) also reported yields from a 9.9-ha field under conservation tillage. Conservation tillage resulted in nutrient loads roughly half as great as for conventional tillage except for dissolved orthophosphorus, which increased from 0.059 to 0.098 tonne km<sup>-2</sup>.

Pennington (2004) reported results of long-term Delta stream water quality sampling program conducted by the USDA-NRCS during 1993--1997 at 22 sites for varying lengths of time. Both N and P concentrations were highly correlated ( $r^2 > 0.78$ ) with suspended sediment concentration and turbidity, and accordingly showed seasonal variation with higher levels in months with higher precipitation and less vegetative cover. Median concentrations of total N and total P in the Sunflower River were about 60% and 100% greater, respectively, during winter than during late summer or fall base flow. Pennington (2004) concluded that erosion control was the key to reducing nutrient levels in Delta streams. Ochs and Milburn (2006) suggested that intentional, managed winter flooding of Delta fields could greatly reduce N export by reducing erosion even though flooding had little net effect on N export due to enhanced denitrification. Maul and Cooper (2000) studied water quality in seasonally flooded agricultural fields and impounded wetlands in the lower delta of the Yazoo Basin and found that sediment containment was essential for nutrient trapping. Others (e.g., Mitsch et al. 2001) have suggested that restoring riparian zones and wetlands that intercept waters moving from cultivated areas to streams might greatly reduce nutrient flux out of agricultural fields. Recent work indicates that restored wetlands may be less efficient nutrient traps than natural wetlands (Hunter and Faulkner 2001, Ullah and Faulkner 2006).

### *Mississippi River*

Transport of P in the Mississippi River is closely related to transport of fine suspended sediments. Accordingly, loads vary seasonally and over longer cycles with discharge. N transport is more complex. Goolsby et al. (1997) note that the flux of N from the Mississippi River to the Gulf of Mexico represents about 13% of the estimated annual N input to the basin from all sources except for soil N. About 60% of the annual flux from the River to the Gulf occurs as nitrate, and the remainder is mostly dissolved and particulate organic N. N levels also follow discharge, with highest levels in spring and early summer. Available data suggest accumulation of N in soils during dry years and release during wet years (Goolsby et al. 1997).

Even though Yazoo Basin yields (tonnes of nutrients per unit land area) are high, loads of N and P leaving the Yazoo Basin tend to comprise a very small fraction (~1-4%) of the load that the Mississippi and Atchafalya Rivers convey to the Gulf because the Yazoo Basin comprises only a small fraction of the area of the Mississippi River

Basin and contributes a small fraction of the total water discharge. Furthermore, N yields are much lower than those for corn-belt watersheds of the Upper Midwest. Kleiss et al. (2000) analyzed nutrient concentrations measured for the Mississippi River at Vicksburg and near the mouth of the Yazoo River during 1995-1998 and found that mean Mississippi River concentrations of total N, nitrate and orthophosphate were 1.8, 3.3, and 1.3 times higher than those mean concentrations near the mouth of the Yazoo.

## Nutrient sinks and transport

### *Nitrogen*

Denitrification is a major sink for N moving through aquatic systems. Denitrification is the process whereby nitrite and nitrate are converted to nitrogen gas through a series of biochemical processes that require a carbon source and anoxic conditions. Denitrification often occurs when nitrate-rich groundwater moves through wetland soils (Lowrance et al. 1995) or streambed sediments (Lefebvre et al. 1995). Coarser sediments have far lower denitrification potential since oxygen concentrations are relatively high in porous beds (Garcia-Ruiz et al. 1998). Alexander et al. (2000) argued that in-stream N loss rates are sharply reduced as water depth increases, and therefore little denitrification occurs in larger rivers as water depth and velocity increase. Interaction between the stream and storage zones such as backwaters and hyporheic zones are also quite important (Runkel 2007). Others reckon that instream N transformation and removal in large rivers is typically low and represents a small percentage of the overall load (Seitzinger 1988). Thus the proximity of the Yazoo Basin to the Mississippi River has led some to suggest that nearly all of the N exiting the basin is delivered to the Gulf (Alexander et al. 2000), but factors such as primary productivity in the lower Mississippi must be evaluated further before definitive statements can be made. More recent large-scale work with tracer isotopes indicates that both large and small streams are both important for retaining and processing excess N (Mulholland et al. 2008). The efficiency of N removal declines as N concentration increases.

Large amounts of N may be removed under ideal conditions in wetlands (Mitsch et al. 2001), forested riparian zones (Lowrance et al. 1995) or in riverine backwaters (James et al. 2007). Loss of these areas to various types of development in the Yazoo Basin may have reduced the potential capacity for denitrification. However, such a reduction likely predate early 1990s since, statistical analysis of N concentration trends at selected sites in the Yazoo Basin by Demcheck and Rebich (2006) indicated no significant trends over the period 1993 to 2003. Denitrification in riparian zones and streambeds is complex, reflecting the influence of hydrologic linkages between surface and groundwaters, local geochemistry, hydraulic conductivity, and the presence of organic carbon and oxygen. Some evidence from studies of specific small streams suggests that channelization and attendant channel incision, which is endemic in the Hills, may reduce denitrification efficiencies of streams and their riparian zones (Kemp and Dodds 2002, Lefebvre et al. 2004, Bohlke et al. 2007), but generalization of these studies to the basin scale is problematic. Whole stream denitrification has been shown to depend on benthic organic matter levels (Kemp and Dodds 2002, Lefebvre et al. 2004), and channel incision in northwest Mississippi is associated with lower bed organic carbon levels relative to nonincised sites (Shields et al. In press).

Stream size and structure, including the presence or absence of riparian zones, backwaters and connected wetlands, govern N transport and processing along streams. Cyclic temporal variations in nitrate-N have been observed in the Mississippi River and its tributaries, with lowest loads in summer and fall and roughly ten times higher

concentrations in late fall, winter and spring (Goolsby and Battaglin 1993). This phenomenon has been attributed to higher rates of plant utilization and lower streamflows in the summer.

The four major flood control reservoirs in the Hills region may serve as seasonal nutrient sinks, but little data were available. Since the impoundments are operated for flood control, runoff from the Hills is captured in late winter and spring when it would otherwise flood downstream Delta lands. After local runoff from the Delta passes downstream, water is gradually released from the large reservoirs. This drawdown process may take all summer and fall. Thus, the reservoirs capture dissolved and particulate nutrients during the period of the year with the greatest runoff and also during spring crop fertilization. N processing may occur in reservoirs through denitrification or biological uptake. As turbidity associated with spring runoff is reduced in the reservoirs, primary productivity increases, and algae consume nitrogen and phosphorus until N becomes limiting in late summer, assuming that unseasonable rainfall does not replenish N. Small impoundments may also serve as N sinks. Cooper and Knight (1990) found that a farm pond had an average “instantaneous” nitrate trap efficiency of 82% during storm events. However, an annual total N budget was not presented. Rausch and Schreiber (1981) found that a small flood detention reservoir in Missouri trapped 36% of the incoming inorganic N during a three-year study.

Lizotte et al. (2001) compared N concentrations in a hill stream with a 37 km<sup>2</sup> mixed cover watershed (<http://ars.usda.gov/Research/docs.htm?docid=5526>) to USEPA nutrient criteria for level III ecoregion 74 streams (US EPA 2000). Criteria based on the 25<sup>th</sup> percentile of measured concentrations in reference streams were 0.364 mg L<sup>-1</sup> TKN, 0.14 mg L<sup>-1</sup> NO<sub>2</sub> + NO<sub>3</sub>, and 0.504 mg L<sup>-1</sup> total N. Total-N concentrations commonly (>80% of samples) exceeded nutrient criteria during storm events. In addition, total N frequently exceeded criteria during base flows. Ammonia-N and nitrate-N rarely (<10% of samples) exceeded published criteria (USEPA 1986), and exceedance instances occurred primarily during storm events.

A numerical water quality model for shallow lakes was recently developed to incorporate the interactions of the N cycle with P, dissolved oxygen, and phytoplankton dynamics based on information taken from a shallow oxbow lake located in the Delta (Chao et al. 2007). Model development was conducted as a research effort aimed at linking physical, chemical, and biological processes in lakes. A secondary goal involved quantifying benefits of agricultural conservation practices at the watershed scale. After calibration and validation of the model using field data from 1999, the effects of varying suspended sediment and nutrient concentrations on lake trophic status, as indicated by chlorophyll concentration, was examined. Chlorophyll levels were extremely sensitive to suspended sediment loading due to light limitations on photosynthesis. A tripling of the observed suspended sediment levels dropped chlorophyll levels to near zero, while a halving of observed suspended sediment triggered increasing mean chlorophyll concentrations by nearly a factor of two. Chlorophyll concentrations were less sensitive to inorganic N levels and insensitive to inorganic P concentrations when nutrient concentrations were varied in the model. Observed suspended sediment levels were used for nutrient sensitivity runs.

## *Phosphorus*

P is found in aquatic systems in either particulate or dissolved forms, and both forms include organic and inorganic fractions. Organic particulates include living biomass such as plankton and dead matter such as detritus. Inorganic particulates include precipitates and P adsorbed to other particulates. P readily sorbs onto iron coatings on clay and other sediments. Dissolved organic P is excreted by organisms and also occurs as colloidal compounds. Soluble inorganic P is usually present in the phosphate compounds  $\text{HPO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , with the distribution among these forms governed by ambient pH. Together, these ions are collectively referred to as soluble reactive P. These compounds are readily available to plants. Because P readily sorbs to sediments and organic particles, P transport is highly correlated with suspended sediment transport, and agriculture is the largest disturbance controlling nonpoint P fluxes from watersheds into channels (FISRWG 1998, Carpenter et al. 1998, Committee 2000). P transport through ecosystems tends to be slower than N transport since it is heavily dependent on erosion and deposition of sediments. Channel bed and bank erosion, such as is common in the Hills of the Yazoo Basin, elevates total P loads in streams, and bank stabilization potentially reduces P loads (Hubbard et al. 2003). P transport varies widely from stream reach to stream reach and with time as it is governed by stream flow, stream velocity and depth, and biochemical processes (Runkel 2007, Doyle et al. 2003). Trend detection analyses showed both unadjusted and flow-adjusted P concentrations were increasing about 10% a year in the Little Tallahatchie River upstream of Sardis reservoir (Demcheck and Rebich 2006), which is located in the Hills (Figure 3).

Reservoirs influence nutrient transport in a variety of ways. P attached to sediment may be removed by settling and sedimentation, and thus may be retained in reservoir sediments for the life of the reservoir (Kennedy and Walker 1990). Dissolved reactive P is likely taken up by primary producers in the four large flood control reservoirs during algal blooms after turbidity is reduced in captured seasonal runoff. Alexander et al. (2008) found that reservoirs exert a major influence on N and P flux throughout the Mississippi River basin, with removals of P much greater than for N. Reservoir nutrient removal efficiency was inversely related to the water flushing rate (Volume of annual inflow/reservoir area).

Farm ponds and small reservoirs are particularly effective P traps, with reported efficiencies of 77% for sediment P and 35% for solution P (Rausch and Schreiber 1981), and about 50% for dissolved orthophosphorus (Schreiber and Rausch 1979). In the Yazoo basin, Cooper and Knight (1990) measured small reservoir efficiency of above 70% for total P and 80% for dissolved orthophosphorus in a farm pond in the hills of the Yazoo Basin, indicating immediate uptake of the orthophosphorus. In 4-7 days after storm events, 0.2 to 0.4 mg L<sup>-1</sup> of dissolved orthophosphorus was typically removed from the water column with a corresponding increase in chlorophyll a.

Total P concentrations in a hill stream with a 37 km<sup>2</sup> mixed cover watershed (<http://ars.usda.gov/Research/docs.htm?docid=5526>) were reported by Lizotte et al. (2001). Total-P concentrations commonly (>80% of samples) exceeded the proposed

criteria (0.75  $\mu\text{g/L}$  TP), which was based on the 25<sup>th</sup> percentile of measured concentrations in reference streams.

A study of Deep Hollow Lake in the Yazoo River Basin during winter revealed that dissolved reactive phosphorus (DRP) in lake water collected at nine locations in the lake from just above the sediments had an average concentration of 0.013  $\text{mg L}^{-1}$ . Pore water DRP of bottom sediments had an average of 0.08  $\text{mg L}^{-1}$  in the upper 3 cm of sediment, while in deeper sediments (5 cm to 20 cm), it decreased (to 0.011  $\text{mg L}^{-1}$  in the 15 to 20 cm layer) (unpublished data, USDA-ARS National Sedimentation Laboratory). Development of a model of the relationship of phosphorus to other water quality parameters in Deep Hollow Lake including nitrogen, dissolved oxygen, and phytoplankton has been reported by Chao et al. (2007).

## Yazoo Basin nutrient yield

### *Estimates based on land use and field scale studies*

The total yields of N and P from Yazoo Basin fields and forests may be roughly estimated by applying the average annual yields reported above for fields and plots to the reported areas for each major land use category as shown in Tables 7 and 8. No specific yield information was found for aquaculture, wetlands, lakes, Delta lowland forests, or Yazoo Basin urban areas. Generally, wetlands capture nutrients during the growing season and slowly release a portion of them during winter. Most Delta lakes that are not part of a chain of waterbodies (such as sloughs and other lakes) have limited seasonal outflow. Unfortunately, no estimates are available for urban storm runoff which may make significant contributions in some watersheds. Failing septic systems are common and can overshadow agricultural runoff as driving factors in nutrient enrichment as was the case with Lake Washington, a Mississippi River oxbow lake south of Greenville in the Delta. Reduction of agricultural nutrient inputs did not relieve eutrophic conditions. When failing septic systems near the lake were corrected, annual hypereutrophication was eliminated. The Lake Washington Project has been highlighted by U. S. EPA as a Nutrient Showcase Project ([www.epa.gov/gmpo/lmrsbc/meetsum\\_lakewa\\_oct03.html](http://www.epa.gov/gmpo/lmrsbc/meetsum_lakewa_oct03.html)).

Average annual yields computed for urban watersheds in central Alabama (McPherson et al. 2003) were used to estimate loads from urban areas in the Yazoo Basin. Loads from cropland were estimated to account for 93% of the total N load and 90% of the total P load. The average annual load of total N reaching Yazoo Basin streams (Table 7) is about half of the average annual load applied to the watershed in the form of manure, chemical fertilizer and atmospheric deposition shown in Table 4. Of course, these estimates are very rough and do not take into account N sources such as eroded soils or legumes. Presumably the difference between applied N and the N load reaching streams is due to removal in the form of crops; storage and processing in field edges, ditches, ephemeral streams, wetlands, ponds, and lakes. Storage and processing may be enhanced by deposition of sediments that contain N in lakes, channels and wetlands. In contrast to N, the estimated average P load reaching Yazoo Basin streams (Table 8) is nearly twice as great as the average mass of P applied to the

watershed in the form of fertilizer or manure as shown in Table 4. The difference may be due to the P input to streams in the form of naturally-occurring P attached to eroding soils, which may contain as much as 1500 mg kg<sup>-1</sup> total P (Yuan et al. 2005). Since sediment yields for the Yazoo Basin watersheds are so high (~1,000 tonne km<sup>-2</sup> yr<sup>-1</sup>, Shields et al. 1995), a soil P content of 350 mg kg<sup>-1</sup> and a sediment yield of 1,000 tonnes km<sup>-2</sup> yr<sup>-1</sup> would provide an annual P input to the channels of about 14,000 tonnes.

### *Nitrogen yield*

Early water quality modeling indicated that about 90% of the N delivered to the Gulf by the Mississippi River is from nonpoint sources, primarily agricultural runoff and atmospheric deposition (Alexander et al. 1997). Only about 1% of the N was estimated to come from point sources such as treatment plants or industries. More recent work shows that only 9% of total N delivered to the Gulf originated from urban sources (Alexander et al. 2008). Estimated average contributions from major basins within the Mississippi River watershed are as shown in Table 9. N yield from the Lower Mississippi River Basin, which includes the Yazoo, was the highest of all of the basins, with an annual average over 2 tonnes km<sup>-2</sup>, accounting for nearly a quarter of the total N flux to the Gulf from the Mississippi River. Slightly different values for subbasin yield were computed by Turner and Rabalais (2004) using the period 1973 – 1994, but both reports noted that although nutrient yields were greatest for the Lower Mississippi River Basin, its share in total flux to the Gulf was relatively low due to its smaller area (Table 9).

More recently published analyses indicated that the total N yield from the Yazoo basin to the Gulf is far lower, between about 0.10 and 0.30 tonne km<sup>-2</sup> yr<sup>-1</sup> (Alexander et al. 2000). Yields from the Midwest were estimated to be as much as an order of magnitude higher. Goolsby and Battaglin (2000) reported that the Yazoo Basin receives moderately high inputs of N but produces relatively low N yield (Figure 8). The latest information released by the US EPA indicates that the upper Mississippi and Ohio-Tennessee River subbasins which include the tile-drained, corn-soybean landscape of Iowa, Illinois, Indiana, and Ohio contribute the lion's share (60% to 80%) of the annual flux of N and P to the Gulf of Mexico (US EPA 2007). In some years, over 50% of the N and P load in the Lower Mississippi River originate in Illinois and Iowa.

Detailed analysis of nutrient flux from the Yazoo Basin has been presented by Runner et al. (2002) and Coupe et al. (undated) who used measurements near the mouth of the Yazoo River to compute annual yields of total N. They found Yazoo Basin total N contributions to the Mississippi were only half as great as the earlier estimates for the Lower Mississippi Basin and for selected watersheds within the Upper Mississippi and Ohio Basins during 1980 – 1996 (Table 10). Using the mean measured load of total N in the Yazoo River for 1996-2004 reported by Coupe (undated), 0.744 tonne km<sup>-2</sup>, and the watershed area of 36,400 km<sup>2</sup>, the mean annual flux of total N is 25,700 tonnes, or about 21% of the mean estimated input in the form of fertilizer and atmospheric deposition (Ruddy et al. 2006). This figure is also about 37% of the total N load reaching Yazoo Basin streams we estimated above (Table 7), highlighting the importance of sites and processes that act as N sinks within the basin.

The average annual loads of total N and nitrate (NO<sub>3</sub>) in the Yazoo River accounted for 1.4 and 0.7 percent, respectively, of the total loads in the Mississippi River during 1996 - 2000. The Yazoo Basin produced 2.8% of the flow of the Mississippi River during the same period (Runner et al. 2002). While Yazoo Basin N is measurable and certainly important, reducing exported N by 30%, a figure suggested by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (2001), would not necessarily produce a measurable N reduction in the Gulf of Mexico.

#### *Phosphorus yield*

Coupe et al. (undated) also used measured water discharges and total P concentrations to compute an estimated mean annual Yazoo Basin P yield of 0.183 tonne km<sup>-2</sup> for the period 1996-2004. Using this figure and the watershed area of 36,400 km<sup>2</sup>, the mean annual flux of total P is 6,330 tonnes, or about 40% of the mean estimated P input to the watershed in the form of fertilizer and atmospheric deposition. This figure is also about 21% of the total P load reaching Yazoo Basin streams we estimated above (Table 8), highlighting the importance of sites and processes such as sediment deposition and storage zones that act as P sinks (Alexander et al. 2008).

The average annual loads of total P and orthophosphorus in the Yazoo River accounted for 3.4 and 1.6 percent, respectively, of the total loads in the Mississippi River during 1996 – 2000 (Runner et al. 2002), reflecting relatively high yield values (Table 11) but relatively small basin size.

## Data

### *FTN survey*

A list of existing water quality data sets for streams, lakes and rivers within the Yazoo Basin was prepared in 2002 – 2003 by a consulting firm under contract to the MDEQ (FTN Associates, Ltd. 2003). The list was provided as an Excel spreadsheet with about 3000 entries describing data available for various geographic locations from various agencies. Each entry represented a single location sampled one or more times. No effort was made by FTN to summarize or analyze the data, and all types of biological, physical, and chemical parameters were included. Analysis of the FTN data base was performed using basic data filter and pivottable tools available within Excel. When the records were filtered to retain only non-duplicated records for nutrient concentrations in water from sites sampled for total P and nitrate at least quarterly or more frequently for at least three years, records for only 112 sites remained. Data for the Delta are sparse relative to the hills. Most data were obtained by the U.S. Geological Survey (24 of 112 sites) or the USDA-ARS National Sedimentation Laboratory (59 of 112 sites).

### *USGS and STORET*

Using our analysis of the FTN data base as a guide, data for surface water nutrient concentrations for sites in the Yazoo River Basin were retrieved from the USGS website (<http://nwis.waterdata.usgs.gov/usa/nwis/qwdata>) using search criteria including site type, location (latitude and longitude of a polygon enclosing the Yazoo River Basin), and parameter codes. A similar retrieval was run using the STORET database websites (legacy (pre 2000) and modern (post 2000) at <http://www.epa.gov/storet/dbtop.html>). Data from only one site and one date were obtained from the modern STORET retrieval, and therefore the analyses described below were based on data from legacy STORET only.

Data from both USGS and STORET were those listed under the following parameter codes:

1. 00625 – total Kjeldahl nitrogen
2. 00630 -- total nitrite plus nitrate in mg L-1 as N
3. 00631 – dissolved nitrite plus nitrate in mg L-1 as N
4. 00620 – total nitrate in mg L-1 as N
5. 00618 – dissolved nitrate in mg L-1 as N
6. 00615 – total nitrite in mg L-1 as N
7. 00613 – dissolved nitrite in mg L-1 as N
8. 00665 -- total phosphorus in mg L-1 as P

Total Kjeldahl N is computed by the USGS as the sum of free ammonia and organic N compounds which are converted to ammonium sulfate during a digestion process. Nitrite plus nitrate values are determined by the USGS by reducing nitrate to nitrite with hydrazine sulfate in an alkaline solution. The sample is then treated with

sulfanilamide under acidic conditions and the resulting red dye is measured using colorimetry (Fishman and Friedman 1989, EPA 353.2 Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction), Revision 2.0, August 1993). USGS total P values are determined by subjecting the sample to persulfate digestion followed by colorimetry (Fishman and Friedman 1989, Patton et al. 2003). The legacy STORET download contained data with agency codes indicating the Vicksburg District of the Corps of Engineers and the Mississippi State Department of Natural Resources (probably the MDEQ), presumably obtained using methods consistent with the USGS since the same parameter codes were applied.

#### *USDA ARS NSL data*

The National Sedimentation Laboratory has collected water grab samples from about 96 sites on streams in 17 Hill watersheds at varying intervals, with earliest collections occurring in 1985. ARS data analyzed for this report were collected between 1985 and 2005. Total Kjeldahl nitrogen as N was measured using digestion and colorimetry, while all other N species measured were limited to dissolved fractions (i.e., samples that were filtered through a 45  $\mu$ m filter). Concentrations of dissolved nitrite (colorimetric method, American Public Health Association 1998) and dissolved nitrate (automated cadmium reduction method, American Public Health Association 1998) were measured using methods that produce results compatible to those of the USGS. Total P methods and measurement units were consistent with those used by others and described above.

## Analysis

### *Total Nitrogen and Nitrate Concentrations*

Total N concentrations were computed using a subset of the available data following an approach similar to that prescribed by Goolsby et al. (1999) and Aulenbach et al. (2007) based on (Rickert 1992). Briefly, if no total Kjeldahl N (TKN, parameter 00625) value was available, no total N value was computed. If TKN was available, then total N was computed as follows:

$$TN = TKN + NO_2 + NO_3$$

where  $NO_2 + NO_3$  was set equal to

1. total  $NO_2 + NO_3$  (00630) if available, and if not
2. dissolved  $NO_2 + NO_3$  (00631) if available, and if not
3. total  $NO_3$  (00620) if available, and if not
4. dissolved  $NO_3$  (00618), and if not
5. then no value of total N was computed.

If total or dissolved  $NO_3$  (00620 or 00618) were used, then total or dissolved  $NO_2$  (00613 or 00615) were added if they were available. This approach is based on the assumption that total  $NO_2 + NO_3$  is dominated by dissolved  $NO_3$ .

This procedure produced total N values for 72 sites with periods of record ranging from 3.3 to 28.6 years. Nineteen of the sites were located in the Delta and 53 were in the Hills. The global mean (mean of site means) total N concentration for the Delta was  $3.3 \text{ mg L}^{-1}$  but only  $1.2 \text{ mg L}^{-1}$  for the Hills. Coefficients of variation for site means (standard deviation of all measurements at a given site divided by the average of all measurements at that site) ranged from 0.4 to 2.1 for the Delta and 0.4 to 1.9 for the Hills. Summary statistics were computed for each site<sup>1</sup>, and scatter plots were prepared showing concentration as a function of contributing drainage area (Figure 9). A total of 35 to 282 samples were available for each Delta site and 35 to 179 were available for each Hill site. Delta sites were either very small streams with drainage areas  $< 10 \text{ km}^2$  or large rivers with drainage areas  $> 1000 \text{ km}^2$ . The smallest Delta sites drained only cultivated fields. Only one Delta site had a drainage area between 10 and  $1000 \text{ km}^2$ . Conversely, Hill sites were concentrated in the 10- $1000 \text{ km}^2$  size class, with only four sites on smaller streams and 8 sites on larger streams. Delta mean and median total N values were negatively correlated with contributing drainage area, and power functions fitted to Delta means and medians plotted well above Hill means and medians (Figure 9 B and C). Only two Hill sites had mean total N concentrations that plotted above the power law curve of concentration as a function of drainage area based on Delta site

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<sup>1</sup> Lists of sites and associated summary statistics for this analysis are provided in digital form (Excel spreadsheets) as appendices.

means. These sites drained an urban watershed (Burney Branch) and the other was within a suburban-rural transitional zone (Mussacuna Creek).

The average concentrations reported here may be compared against regional criteria for rivers and streams developed by the US EPA under Section 304 of the Clean Water Act (US EPA 2000 and 2001). The Delta portion of the Yazoo Basin is part of aggregated Ecoregion X, while the Hills are part of aggregated Ecoregion IX. Total N criteria are  $0.69 \text{ mg L}^{-1}$  for the Hills and  $0.76 \text{ mg L}^{-1}$  for the Delta (US EPA undated).

Some form of nitrate was reported for a slightly larger number of sites than those for which total N values were computed (which required TKN and some form of nitrate, as described above). Total  $\text{NO}_2 + \text{NO}_3$  concentrations were developed as follows. Total  $\text{NO}_2 + \text{NO}_3$  was assumed equal to

6. total  $\text{NO}_2 + \text{NO}_3$  (00630) if available, and if not
7. dissolved  $\text{NO}_2 + \text{NO}_3$  (00631) if available, and if not
8. total  $\text{NO}_3$  (00620) if available, and if not
9. dissolved  $\text{NO}_3$  (00618), and if not
10. then no value of  $\text{NO}_2 + \text{NO}_3$  was computed.

If total or dissolved  $\text{NO}_3$  (00620 or 00618) were used, then total or dissolved  $\text{NO}_2$  (00613 or 00615) were added if they were available. This approach is based on the assumption that total  $\text{NO}_2 + \text{NO}_3$  is dominated by dissolved  $\text{NO}_3$ . For purposes of this analysis, values reported as less than detection limits (either  $< 0.2$  or  $< 0.1 \text{ mg L}^{-1}$ ) were set equal to 0.5 times the detection limit.

Statistics for nitrate concentration were computed for 114 sites with periods of record ranging from 3.2 to 19.8 years. Twelve sites were in the Delta and 112 were in the Hills. Global means were  $1.7 \text{ mg L}^{-1}$  for the Delta (about half of the total N mean) and  $0.34 \text{ mg L}^{-1}$  for the Hills (about one-fourth of the total N mean). As for total N, scatter plots of concentration versus drainage area were prepared (Figure 9). Nine Delta sites were from small streams with drainage areas  $< 10 \text{ km}^2$ , and three were from large rivers with drainage areas  $> 1000 \text{ km}^2$ , but none were from intermediate sized sites. The smallest Delta sites drained only cultivated fields. Ninety-three of the 102 Hill sites were from intermediate-sized ( $10\text{-}1000 \text{ km}^2$ ) drainage areas. Each site was sampled between 45 and 638 times. As for total N, Delta mean and median total N values were negatively correlated with contributing drainage area, and power functions fitted to Delta means and medians plotted well above Hill means and medians (Figure 9 B and C).

Total N concentrations were examined for seasonality by plotting mean concentration (averaged across all sites and through all time) versus month of the year for Delta and Hill sites (Figure 10A). In this case, only data from months and sites where at least six values existed were used in computing monthly means. Delta mean total N concentrations were higher throughout the year and exhibited strong seasonal behavior similar to that reported by Pennington (2004) for TKN at 22 sites on Delta rivers sampled between 1992 and 1997. Pennington (2004) reported peak concentrations in April that smoothly declined to a minimum in August, while our

computations showed peak levels occurred slightly later (in April) and increasing concentrations in late Fall. The elevated concentrations in December were due to high concentrations measured in small ditches draining croplands and coincided with the onset of rainy weather after the August-October dry season. Hill total N levels fluctuated about  $1 \text{ mg L}^{-1}$  and exhibited no seasonality. Much higher (up to  $23 \text{ mg L}^{-1}$ ) monthly average total N levels were computed for small channels (watershed sizes  $0.1 - 6 \text{ km}^2$ ) draining experimental watersheds in the Delta (Rebich 2004); these sites are not reflected in the monthly means shown in Figure 10A.

Nitrate levels were also examined for seasonality by plotting mean concentration (averaged across all sites and through all time) versus month of the year for Delta and Hill sites (Figure 10B). As for total N, only data from months and sites where at least six values existed were used in computing monthly means. Delta mean total  $\text{NO}_2 + \text{NO}_3$  concentrations were higher than Hill concentrations except for two months in the Fall. Delta levels varied seasonally, with monthly mean total  $\text{NO}_2 + \text{NO}_3$  peaking near  $1.0 \text{ mg L}^{-1}$  in May and gradually declining to less than 40% of peak level by September. Although Delta monthly nitrate means peaked at about the same time as total N, they were only about 30 to 40% as great as total N. This may indicate that much of the N that is transported in Delta streams and rivers is in association with suspended sediment rather than as dissolved nitrate. Nitrate-N levels were generally lower than those reported for several Mississippi River tributaries in the Midwest by Goolsby and Battaglin (1993).

#### *Total Phosphorus Concentrations*

Total P concentration data for sites for which there were fewer than 30 samples were excluded from this analysis, leaving data from 121 sites with periods of record ranging from 3.2 to 28.6 years. Summary statistics were computed for each site, and scatter plots were prepared showing concentration as a function of contributing drainage area (Figure 11). Between 45 and 643 samples were collected from each Hill site, while Delta sites were sampled 70 to 367 times each (Figure 11A). Only two Delta sites had contributing drainage areas between 10 and  $1000 \text{ km}^2$ , but only 9 Hill sites fell outside this interval. Delta P concentrations were inversely proportional to contributing drainage area, while Hill sites were not. Hill P means (Figure 11B) and medians (Figure 11C) plot below regression lines for Delta P on concentration versus drainage area scatter plots, indicating the overall lower values observed there. In fact, only one Hill site mean plots above the power law curve of concentration as a function of drainage area based on Delta site means (Figure 11B), and it is from a site draining an urban watershed (Burney Branch). Mean total P for Burney Branch was  $1.29 \text{ mg L}^{-1}$ , about 4 times greater than the next greatest Hill site mean. The Hill grand mean P concentration was  $0.15 \text{ mg L}^{-1}$  while the grand mean for Delta sites was more than four times greater,  $0.66 \text{ mg L}^{-1}$ . Variations in observed P concentrations were within expected limits, with coefficients of variation for Delta sites ranging from 0.39 to 2.00 and for Hill sites from 0.65 to 2.55. Highest levels of median total P occurred at sites receiving runoff from small ( $\sim 0.2 \text{ km}^2$ ), cultivated watersheds in the Delta while lowest median levels were found at Hill sites that drained forested watersheds between 10 and  $20 \text{ km}^2$  in size.

The average concentrations reported here may be compared against published recommended criteria for rivers and streams (US EPA 2000 and 2001). Total P criteria are 0.0356 mg L<sup>-1</sup> for the Hills and 0.128 mg L<sup>-1</sup> for the Delta (US EPA undated). The criteria value for the Delta has been flagged as inordinately high, and the US EPA has recommended further study to determine if it reflects measurement error, notational error, statistical anomaly, natural enriched conditions, or cultural impacts.

Total P concentrations were also examined for seasonality by plotting mean concentration (averaged across all sites and through all time) versus month of the year for Delta and Hill sites (Figure 12). In this case, only data from months and sites where at least six values existed were used in computing monthly means. Delta mean total P concentrations were higher throughout the year and exhibited strong seasonal behavior quite similar to that reported by Pennington (2004) for 22 sites on Delta rivers sampled between 1992 and 1997. Pennington (2004) reported peak concentrations in April that smoothly declined to a minimum in September, while our computations showed peak levels occurred slightly later (in May), concurrent with total N and nitrate peaks. Hill total P concentrations did not display seasonal patterns.

### *Loads*

Development of load estimates using mean daily water discharge records and grab-sample nutrient concentrations is a complex process (Runkel et al. 2004). An attempt was made to derive nutrient concentration rating curves using data from about 23 sites with concurrent discharge and nutrient data in order to estimate loads, but this was not successful. Further analysis of loads is beyond the scope of this study.

## **Summary and conclusions**

Elevated levels of nutrients in aquatic ecosystems are an increasing worldwide problem. Elevated P levels pose the greatest hazard to freshwater systems, while marine systems, in particular the Gulf of Mexico, are normally N-limited. Most of the increase in nutrient loadings to aquatic systems in the last 40 years can be attributed to the increased use of agricultural fertilizers.

Within the Yazoo Basin, nutrient transport differs widely for the two major physiographic regions (Delta and Hills). Concentrations of total N and nitrate in the Delta peak strongly in the Spring (May) when agricultural fertilizers are applied and runoff occurs from bare, tilled soil. Total P concentrations in the Delta peak in Spring (May), corresponding to periods of higher runoff and again in later summer for unknown reasons. Concentrations of N and P in Hill streams do not exhibit seasonal trends, but tend to be one third to two thirds as great as the Delta levels. Concentrations in Delta streams tend to decrease with increasing watershed size, perhaps reflecting dilution from Hill tributaries, instream retention and processing, or as an anomaly of the available data, since the only small Delta watersheds that have been monitored were intensely cultivated.

Yields of N and P from the Yazoo basin to the Lower Mississippi River are about 37% and 21%, respectively, of the estimated loads that are input to Yazoo basin streams. The difference between the amount of N and P that are input to the basin as fertilizer, manure, and atmospheric deposition and the amount that reaches the Mississippi River highlights the importance of processes such as sedimentation, denitrification and uptake that occur in lakes, streams and wetlands.

## **Acknowledgments**

Dean Pennington and Molly Davis reviewed an earlier version of this report and made many helpful comments.

# FIGURES

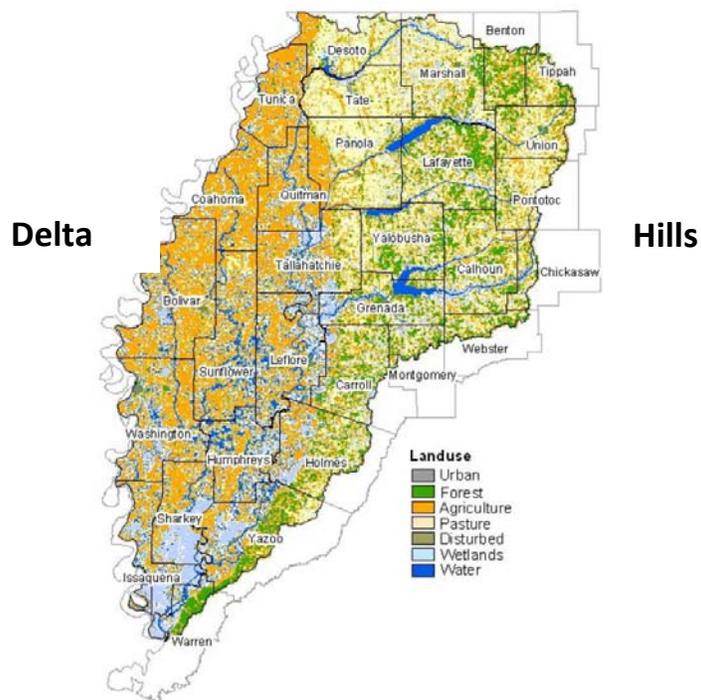


Figure 1. Major Land Uses in the Yazoo River Basin. From Guedon and Thomas (2004)

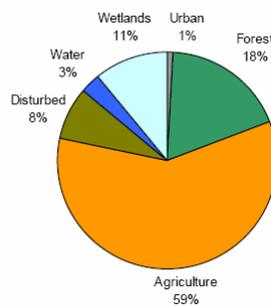
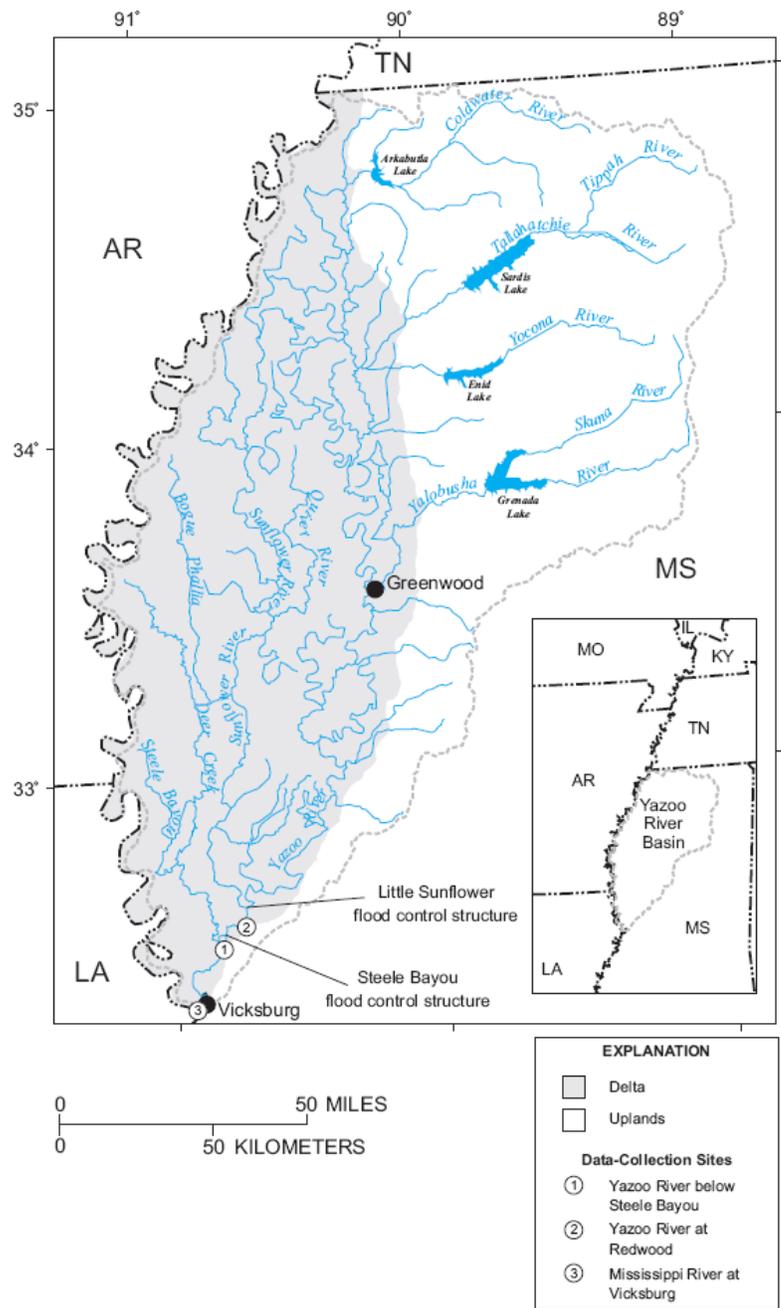
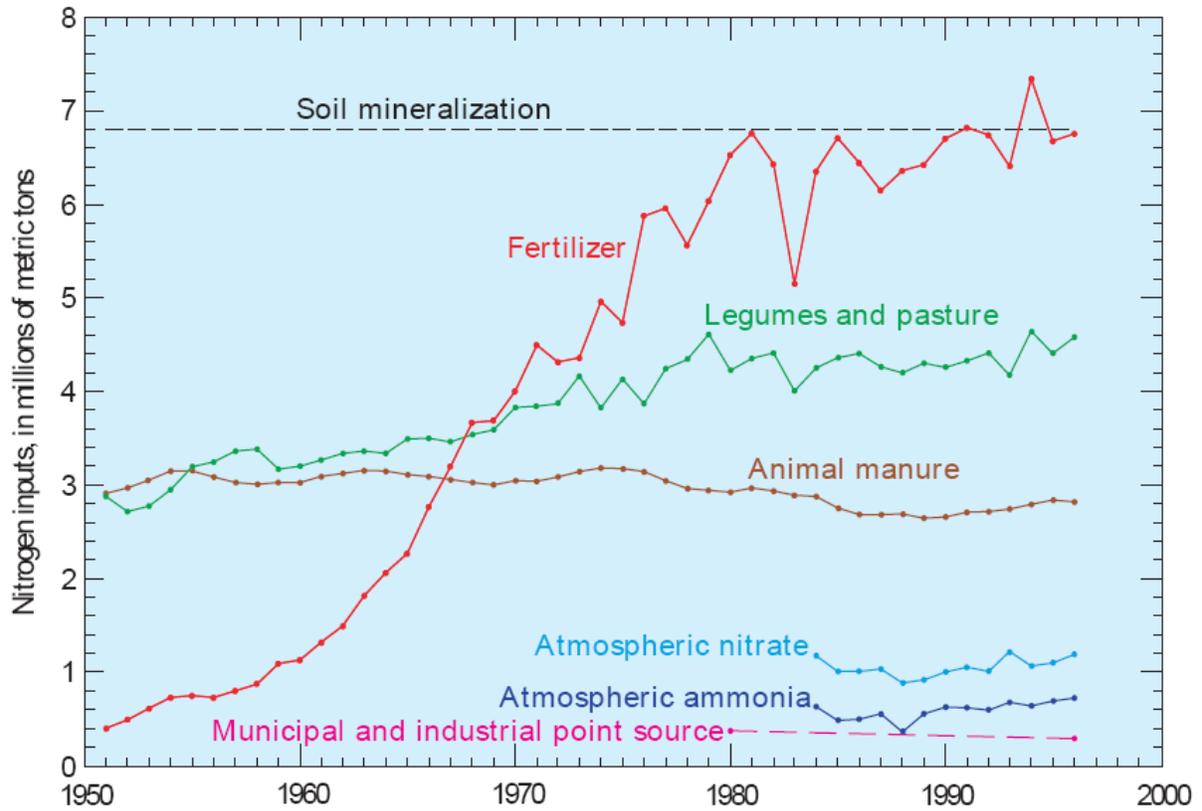


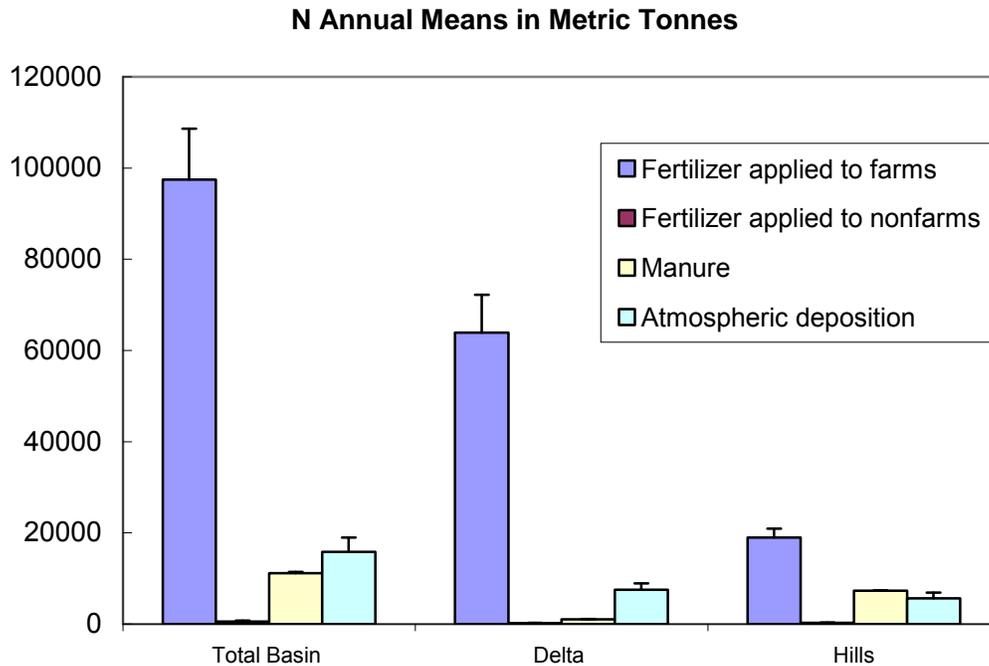
Figure 2. Land Use Distribution in the Yazoo River Basin. From Guedon and Thomas (2004)



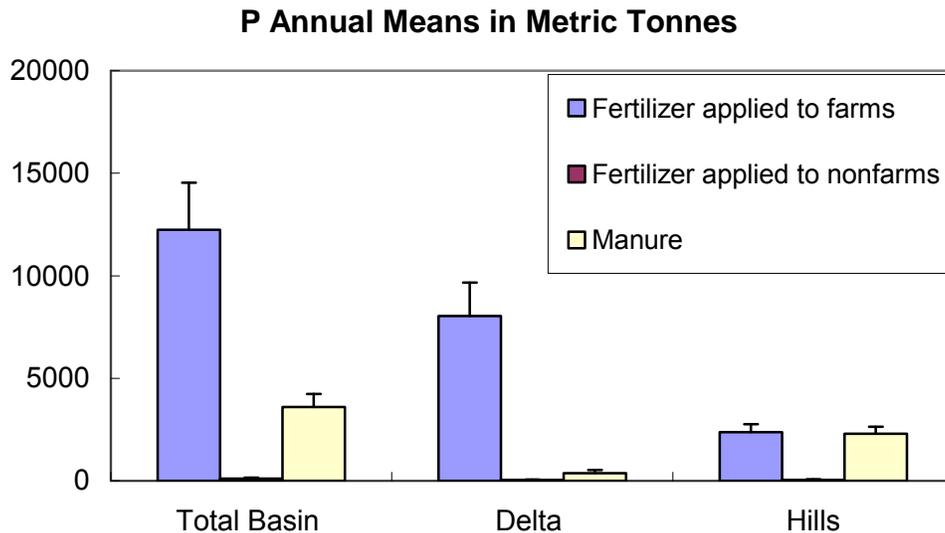
**Figure 3. Major rivers and reservoirs of the Yazoo River Basin. From Runner et al. (2002).**



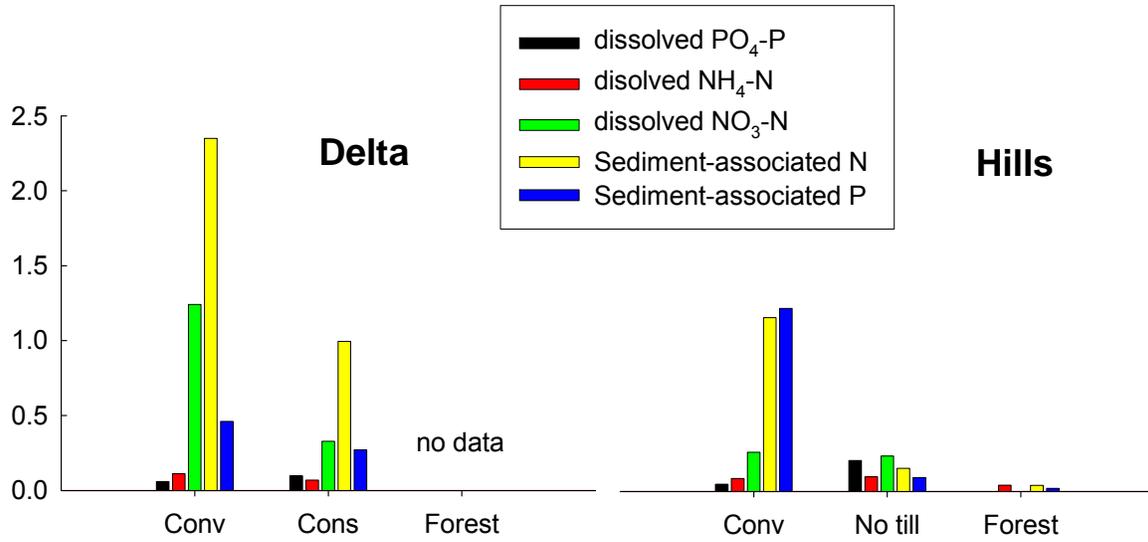
**Figure 4. Annual nitrogen inputs to the Mississippi Basin from major sources. From Goolsby and Battaglin (2000)**



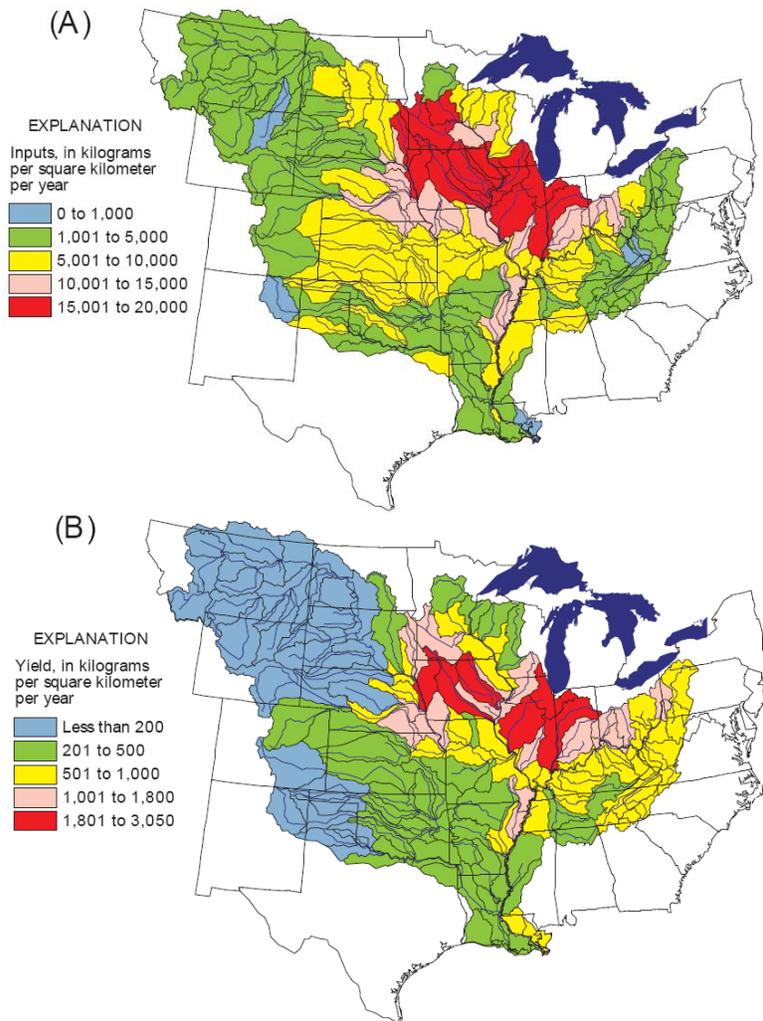
**Figure 5. Estimated average annual total nitrogen input to the Yazoo River Basin from fertilizer, manure and atmospheric deposition, 1981-2001. Error bars represent one standard deviation. Based on data from Ruddy et al. (2006).**



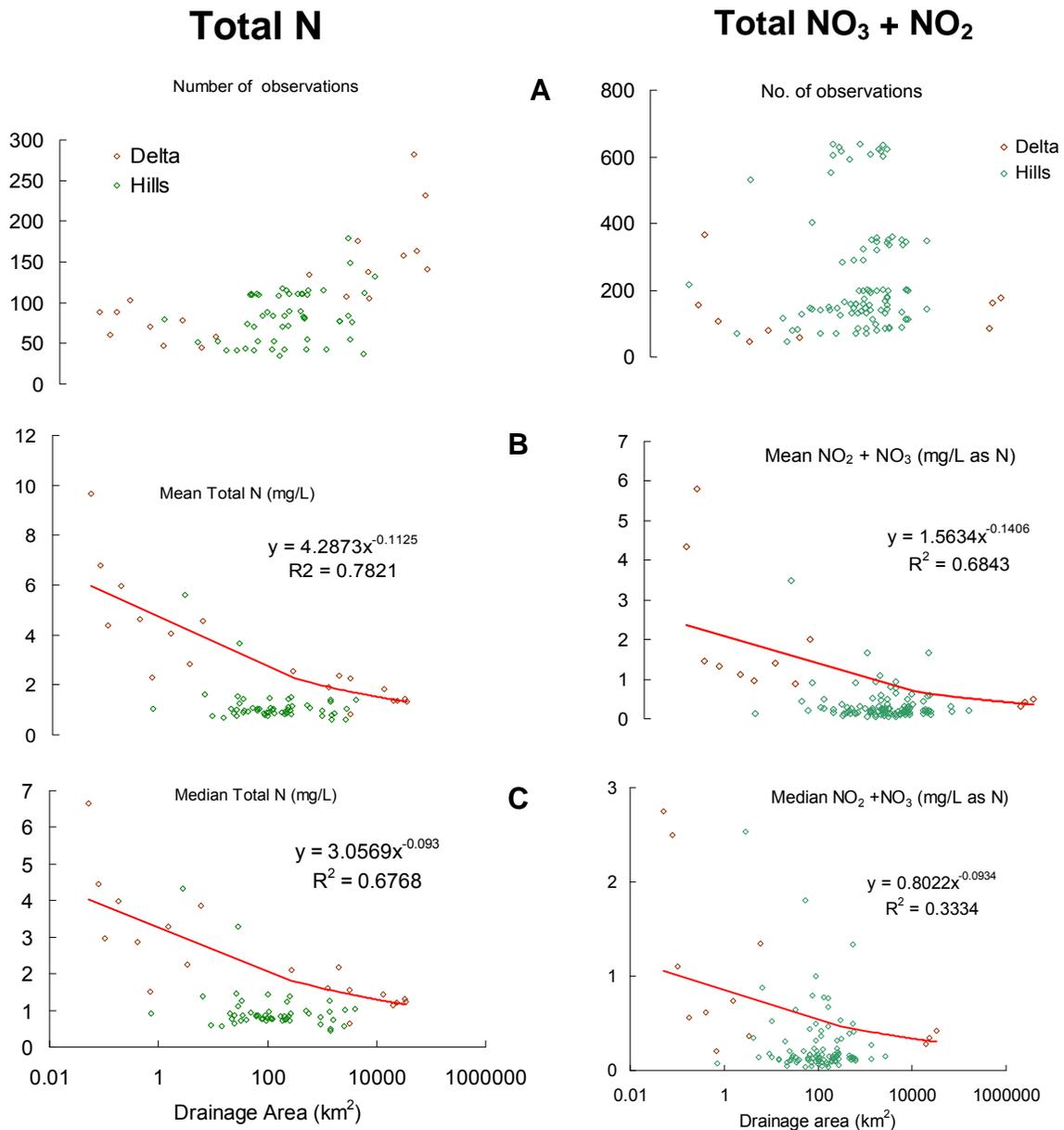
**Figure 6. Estimated average annual total phosphorus input to the Yazoo River Basin from fertilizer, manure and atmospheric deposition, 1981-2001. Error bars represent one standard deviation. Based on data from Ruddy et al. (2006).**



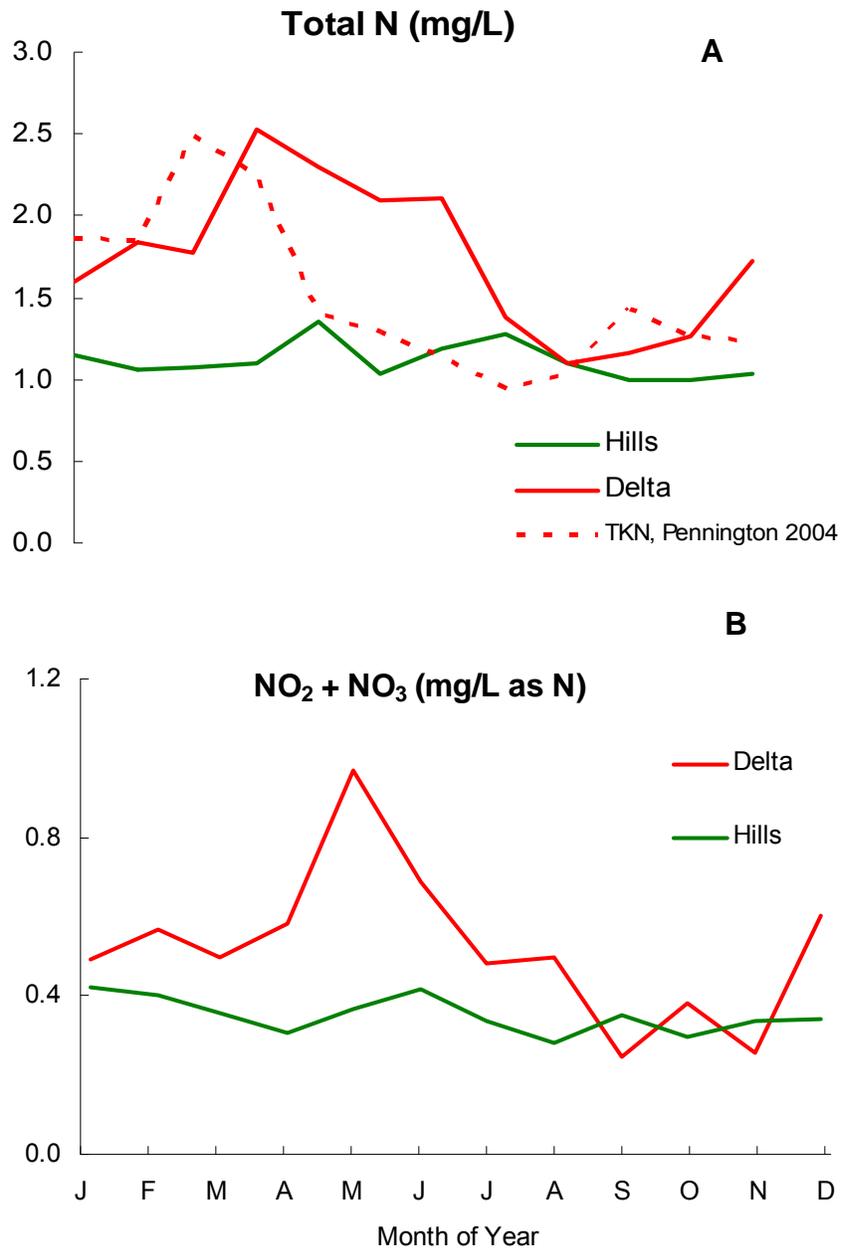
**Figure 7. Mean annual nutrient yields in tonne km<sup>-2</sup> from conventionally-tilled fields, no-till fields and forested study watersheds in the Hills and Delta. Data from Schreiber et al. 2001.**



**Figure 8. (A) Nitrogen inputs during 1992 and (B) average annual N yields of streams for 1980-1996. From Goolsby and Battaglin (2000).**

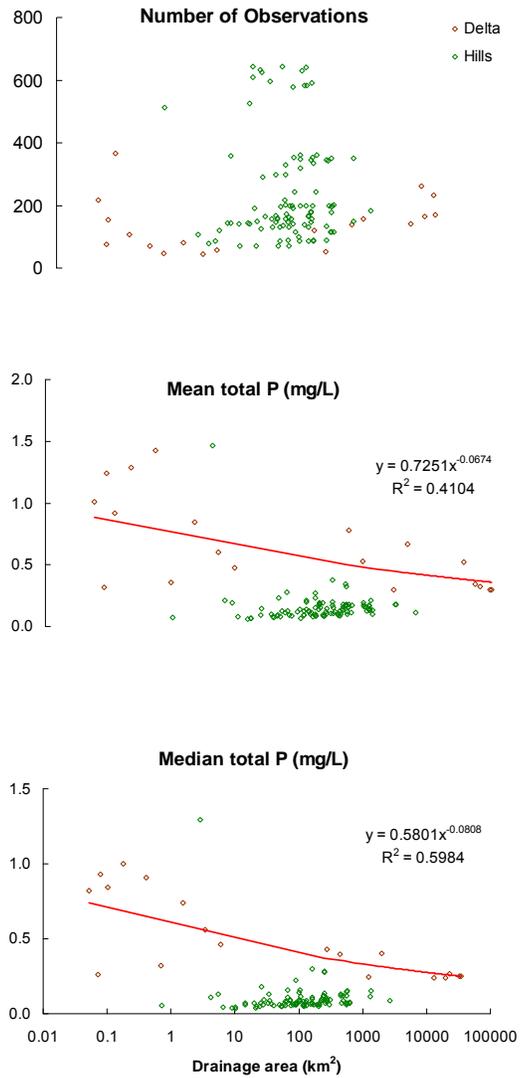


**Figure 9. Nitrogen concentrations in mg L<sup>-1</sup> versus contributing drainage area for sites along streams in the Yazoo Basin. A) Number of samples, B) Mean concentration, and C) Median concentration. Values of Total N and NO<sub>3</sub> + NO<sub>2</sub> determined as described in text. Red curves are regressions based on Delta data only.**

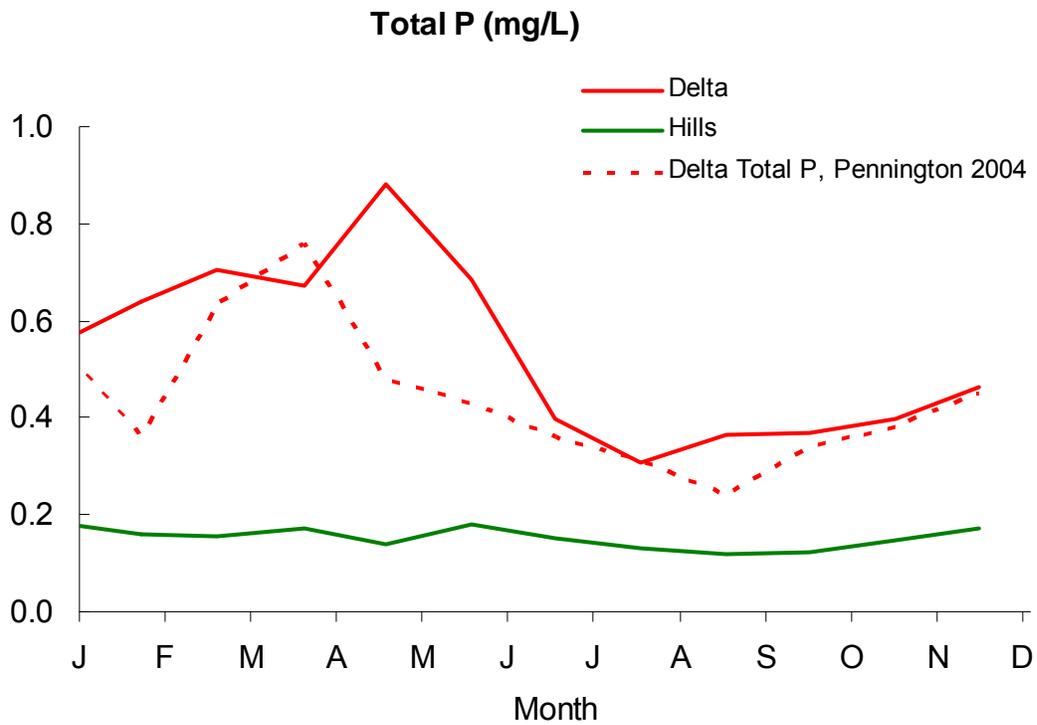


**Figure 10. Mean (A) total nitrogen and (B) nitrate concentrations for each month for stream sites in the Yazoo Basin. Values of total N and NO<sub>2</sub> + NO<sub>3</sub> determined as described in the text.**

## Total P



**Figure 11. Total phosphorus concentrations in mg L<sup>-1</sup> versus contributing drainage area for sites along streams in the Yazoo Basin. A) Number of samples, B) Mean concentrations, and C) Median concentrations.**



**Figure 12. Mean total phosphorus concentrations for each month for stream sites in the Yazoo Basin.**

# TABLES

**Table 1. Approved TMDLs for Delta waterbodies impaired by excessive nutrient levels**

Waterbody Name	Pollutant of Concern	Final Approval Date
Bear Creek Watershed	Organic Enrichment / Low DO and Nutrients	30-Jun-03
Bee Lake	Organic Enrichment / Low DO, Nutrients, and Sediment / Siltation	30-Jun-03
Big Sunflower River	Organic Enrichment / Low DO, Nutrients, and Sediment / Siltation	30-Jun-03
Black Bayou	Organic Enrichment / Low DO and Nutrients	30-Jun-03
Coldwater River	Organic Enrichment / Low DO and Nutrients	24-Jun-03
Deer Creek	Organic Enrichment / Low DO and Nutrients	23-Jun-03
Dump Lake	Organic Enrichment / Low DO, Nutrients, and Sediment / Siltation	30-Jun-03
Hickahala and Senatobia Creeks	Organic Enrichment / Low DO and Nutrients	23-Jun-03
Hurricane Creek	Organic Enrichment / Low DO and Nutrients	23-Jun-03
Lake Washington	Organic Enrichment / Low DO, Nutrients, and Sediment / Siltation	1-Sep-03
Moorhead Bayou	Organic Enrichment / Low DO and Nutrients	30-Jun-03
Wolf Lake	Nutrients and Sediment / Siltation	01-Sep-03

**Table 2. Data sources for nutrient estimates (Ruddy et al. 2006)**

Source	Data	Time Period	Scale
Association of American Plant Food Control Officials	Fertilizer sales	Annually, 1987 through 2001	State and County
Census of Agriculture	Expenditures on fertilizer; livestock population	1982, 1987, 1992, 1997, and 2002	State and County
U.S. Census Bureau	Human Population	1990 and 2000 (actual); 1987-89, 1991-99, and 2001 estimated	County
National Atmospheric Deposition Program	Wet deposition chemistry	Annually, 1985 through 2001	Point Locations

**Table 3. Average annual N and P inputs to the Yazoo River Basin by county (adapted from Ruddy et al. 2006).**

County	Region	Area (km <sup>2</sup> )	Annual Means			
			Total N (10 <sup>5</sup> kg)	Total P (10 <sup>5</sup> kg)	Mean Annual N Input (kg/km <sup>2</sup> )	Mean Annual P Input (kg/km <sup>2</sup> )
Bolivar	Delta	2345.89	106.671	12.343	4547.13	526.14
Calhoun	Hills	1522.84	45.272	5.945	2972.89	390.38
Carroll	Hills	1643.47	40.137	6.277	2442.21	381.95
Coahoma	Delta	1510.35	74.467	8.646	4930.44	572.45
Desoto	Hills	1286.64	40.217	5.879	3125.74	456.9
Grenada	Hills	1163.88	23.556	3.363	2023.89	288.93
Holmes	Both	1979.22	60.521	7.822	3057.83	395.23
Humphreys	Delta	1116.75	47.389	5.446	4243.47	487.7
Issaquena	Delta	1143.13	28.395	3.097	2483.94	270.89
Lafayette	Hills	1759.32	24.27	3.185	1379.52	181.04
Leflore	Delta	1570.47	77.103	9.043	4909.53	575.8
Marshall	Hills	1838.38	45.49	6.897	2474.48	375.15
Panola	Hills	1826.28	60.966	8.698	3338.25	476.25
Quitman	Delta	1052.85	43.432	4.936	4125.22	468.86
Sharkey	Delta	1126.36	46.436	5.317	4122.64	472.08
Sunflower	Delta	1831.69	84.636	9.873	4620.68	539.01
Tallahatchie	Delta	1688.91	79.78	9.935	4723.78	588.23
Tate	Hills	1064.36	41.03	6.835	3854.93	642.19
Tunica	Delta	1245.24	48.286	5.484	3877.66	440.41
Union	Hills	1079.72	27.258	3.951	2524.51	365.94
Washington	Delta	1971.67	90.336	10.516	4581.68	533.35
Yalobusha	Hills	1282.06	22.265	3.059	1736.64	238.63
Yazoo	Both	2419.38	96.623	12.937	3993.73	534.74

**Table 4. Estimated average annual N and P inputs to the Yazoo River Basin from fertilizer, manure and atmospheric deposition in metric tonnes.**

Source	N	P
Atmospheric Deposition	15,507	
Fertilizer applied to farms	95,389	11,988
Fertilizer applied to nonfarms	527	105
Livestock Manure	12,085	3,596
Grand Total	123,507	15,689

**Table 5. Percentage of estimated average annual N and P inputs to the Yazoo River Basin by source and region. Inputs are exclusive of crop N fixation, point sources, and soil erosion. Based on data from Ruddy et al. (2006)**

Nutrient	Source	Delta	Hills	Totals
N	Atmospheric Deposition	7	6	13
	Fertilizer applied to farms	56	21	77
	Fertilizer applied to nonfarms	0.2	0.2	0.4
	Livestock Manure	2	8	10
	Totals	65	35	100
P	Fertilizer applied to farms	55	21	86
	Fertilizer applied to nonfarms	0.3	0.3	0.6
	Livestock Manure	5	18	23
	Totals	61	39	100

**Table 6. Annual mean nitrogen and phosphorus yields in tonnes km<sup>-2</sup> from an 18.7-ha watershed planted to cotton in the Delta region of the Yazoo River Basin 1973 – 1979. From McDowell et al. (1989)**

Nutrient	Soluble form	Associated with sediment	Total yield
Nitrogen	0.77	3.46	4.23
Phosphorus	0.16	1.96	2.12

**Table 7. Estimated average annual total N load delivered to Yazoo Basin streams**

Region	Land use	Area (km <sup>2</sup> )	Estimated average annual yield (tonne/km <sup>2</sup> )	Reference	Estimated average annual load (tonnes)
Hills, total N	forest	8,466	0.043	Schreiber et al. 2001	364
	pasture	5,312	0.3	Assumed	1,594
	cropland	2,158	2.0	McDowell and McGregor 1980 and 1984, Schreiber et al. 2001	4,316
	urban	166	0.11	McPherson et al. 2003	19
	water/lakes	332	0.1	Assumed	33
	wetland	166	0.1	Assumed	17
Delta, total N	forest	3,420	0.043	Schreiber et al. 2001	147
	pasture	900	0.3	Assumed	270
	cropland	11,520	4.2	McDowell et al. 1989	48,732
	urban	180	0.11	McPherson et al. 2003	20
	water/lakes	540	0.1	Assumed	54
	wetland	900	0.1	Assumed	90
	aquaculture	540	1.0	Assumed	540
Totals		34,600			56,195

**Table 8. Estimated average annual total P load delivered to Yazoo Basin streams**

Region, nutrient	Land use	Area (km <sup>2</sup> )	Estimated average annual yield (tonne/km <sup>2</sup> )	Reference	Estimated average annual load (tonnes)
Hills, total P	forest	8,466	0.024	Schreiber et al. 2001	203
	pasture	5,312	0.50	Assumed	1,594
	cropland	2,158	1.0	McDowell and McGregor 1980 and 1984, Schreiber et al. 2001	2,158
	urban	166	0.014	McPherson et al. 2003	0.2
	water/lakes	332	0.1	Assumed	33
	wetland	166	0.1	Assumed	17
Delta, total P	forest	3,420	0.024	Schreiber et al. 2001	81
	pasture	900	0.5	Assumed	450
	cropland	11,520	2.12	McDowell et al. 1989	24,423
	urban	180	0.014	McPherson et al. 2003	0.3
	water/lakes	540	0.1	Assumed	54
	wetland	900	0.1	Assumed	90
	aquaculture	540	1	Assumed	540
Totals		34,600			29,649

**Table 9. Estimated mean annual total N flux to the Gulf of Mexico from the Mississippi River by subbasin, tonnes km<sup>-2</sup>**

Basin	1975 – 1995 (Alexander et al. 2008)	1985 - 1988 (Alexander et al. 1997)	1973 - 1994 (Turner and Rabalais 2004)
Missouri	0.135	0.083	0.140
White/Arkansas	0.189	0.108	0.141
Ohio	0.959	0.437	0.765
Upper Mississippi	0.402	0.708	1.120
Central Mississippi River	1.282	1.652	nd
Lower Mississippi River	0.651	2.072	1.712

**Table 10. Comparison of reported average annual yields, tonnes km<sup>-2</sup>**

Watershed	Time period	Total N	NO <sub>3</sub> - N	Reference
Lower Mississippi River	1985 - 1988	2.072		Alexander et al. 1997
Lower Mississippi River	1973 - 1994	1.712		Turner and Rabalais 2004
Minnesota River	1980 - 1996	1.280	1.200	Goolsby 1999
Iowa River	1980 - 1996	2.290	1.770	Goolsby 1999
Yazoo River	1980 - 1996	0.605	0.295	Goolsby 1999
Yazoo River	1996 - 2000	0.660	0.136	Runner et al. 2002
Yazoo River	1996 - 2004	0.744	0.183	Coupe et al. undated

**Table 11. Estimated mean annual yields of P from Mississippi River subbasins in (from Alexander et al. 2008)**

Basin	P Yield, tonnes km <sup>-2</sup>
Missouri	0.008
White/Arkansas	0.019
Ohio/Tennessee	0.075
Upper Mississippi	0.027
Central Mississippi River	0.086
Lower Mississippi River	0.077

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