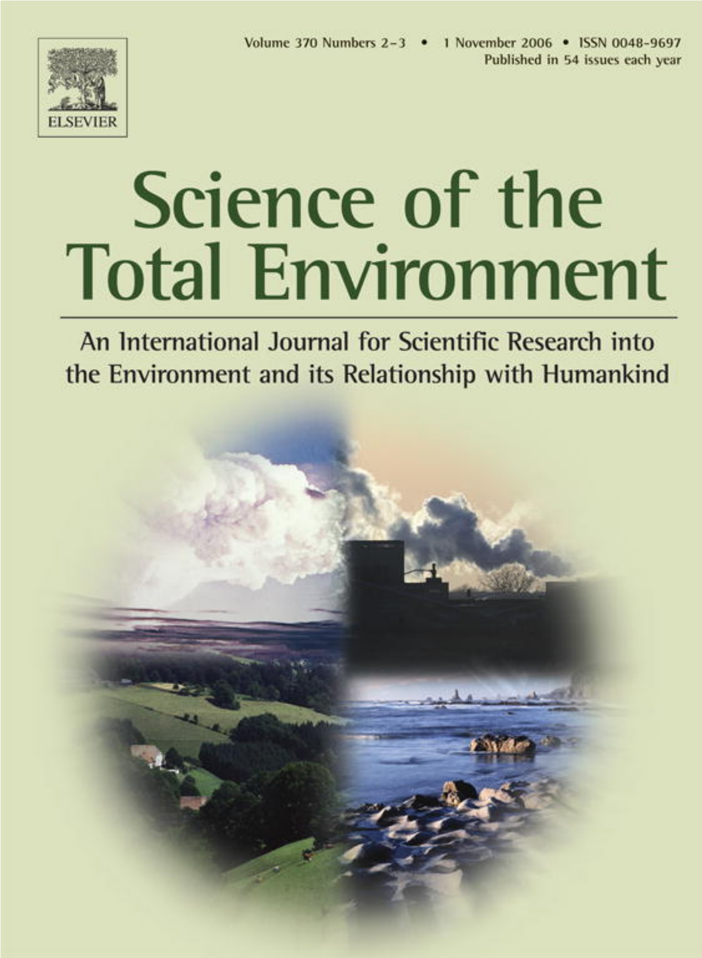
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Influence of watershed system management on herbicide concentrations in Mississippi Delta oxbow lakes

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Abstract

The Mississippi Delta Management Systems Evaluation Area (MD-MSEA) project was established in 1994 in three small watersheds (202 to 1497 ha) that drain into oxbow lakes (Beasley, Deep Hollow, and Thighman). The primary research objective was to assess the implications of management practices on water quality. Monthly monitoring of herbicide concentrations in lake water was conducted from 2000 to 2003. Water samples were analyzed for atrazine, cyanazine, fluometuron, metolachlor, and atrazine metabolites. Herbicide concentrations observed in the lake water reflected cropping systems of the watershed, e.g., atrazine and metolachlor concentrations were associated with the level of corn and sorghum production, whereas cyanazine and fluometuron was associated with the level of glyphosate-sensitive cotton production. The dynamics of herbicide appearance and dissipation in lake samples were strongly influenced by herbicide use, lake hydrology, rainfall pattern, and land management practices. The highest maximum concentrations of atrazine (7.1 to 23.4 μg L^{-1}) and metolachlor (0.7 to 14.9 μg L^{-1}) were observed in Thighman Lake where significant quantities of corn were grown. Introduction of *s*-metolachlor and use of glyphosate-resistant cotton coincided with reduced concentration of metolachlor in lake water. Cyanazine was observed in two lakes with the highest levels (1.6 to 5.5 μg L^{-1}) in 2000 and lower concentrations in 2001 and 2002 (<0.4 μg L^{-1}). Reduced concentrations of fluometuron in Beasley Lake were associated with greater use of glyphosate-resistant cotton and correspondingly less need for soil-applied fluometuron herbicide. In contrast, increased levels of fluometuron were observed in lake water after Deep Hollow was converted from conservation tillage to conventional tillage, presumably due to greater runoff associated with conventional tillage. These studies indicate that herbicide concentrations observed in these three watersheds were related to crop and soil management practices.

Keywords: Atrazine; Cyanazine; Fluometuron; Herbicides; Metolachlor; Mississippi Delta; Oxbow lakes; Water quality

1. Introduction

For environmental quality assessments of agricultural management, watershed studies provide an opportunity for scientists to measure the effects of management practices at a large scale and as integrated systems. The primary goal of an ideal environmental watershed study

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is to obtain a comprehensive and systematic appraisal of agricultural management within the entire watershed. For a watershed evaluation to be completely successful, it is often necessary to evaluate individual components of the watershed management systems. One of many major challenges in conducting watershed studies, however, is to isolate cause–effect relationships. Another challenge in evaluating these systems is that of replication. It is extremely costly to replicate experimental treatments at even field scales, and there may be some question as to whether exact replication is possible at watershed scales. A third challenge is that many watersheds under evaluation are managed by private landowners or tenants, and it is difficult to maintain long-term, consistent management inputs within watersheds to assess trends.

In the early 1990s, USDA implemented watershed studies in several Midwestern states under an umbrella project called Management Systems Evaluation Areas (MSEA). History and background of the Midwestern MSEA Project is reported elsewhere (Ward et al., 1994; Hatfield et al., 1999). Information accumulated in these projects have provided useful information on the role of agricultural management practices in controlling movement of herbicides to surface waters (Jaynes et al., 1999). An overall purpose of the Midwestern MSEA Project was to assess the effects of recommended or best agricultural management practices (BMPs) on water quality. The Midwestern MSEA projects faced some of the challenges mentioned previously, in that they involved large watersheds, private landowners, and often there were few common threads of comparisons from watershed to watershed. In the second phase of this national assessment of the effects of best management practices on water quality, the USDA Agricultural Research Service and partners expanded research into the Mississippi Delta as the Mississippi Delta Management System Evaluation Area (MD-MSEA) Project in 1994. Background information on the MD-MSEA project was reported in Locke (2004).

The Mississippi project was designed with three small oxbow lake watersheds (202 to 1497 ha), each with successively increasing degrees of BMP implementation to overcome difficulties faced in the Midwestern MSEA studies. This provided an opportunity for comparison of management systems from watershed to watershed. Another major difference between the MD-MSEA and Midwestern MSEA projects is that the Mississippi Delta project was based on small watersheds that drain into oxbow lakes; the Midwestern projects focused on watersheds that drained into creeks and streams. A third distinction was that the Mississippi project was designed to focus on watersheds with a majority of the acreage under a cotton cropping system, while the Midwestern project involved corn and soybean cropping systems.

The Mississippi Delta is an area of intensive agriculture production historically dominated by cotton production, with significant land use under soybean, rice, corn, and catfish production. The warm humid climate often necessitates extensive use of fertilizers and pesticides to enhance crop production. The enclosed watersheds allowed monitoring of environmental effects resulting from different management practices in these areas. One of the major cotton herbicides of interest at the outset of the Mississippi project was fluometuron, which was used extensively as a soil-applied herbicide in cotton. Herbicide concentrations measured in the Mississippi oxbow lakes from 1996 to 1999 were reported in Zablotowicz et al. (2004), and results from the first 4 years of study indicated that fluometuron and its metabolite des-methyl fluometuron were observed in oxbow lake water when conventional cotton was planted. Similar levels of herbicides were detected in Mississippi Delta streams with the levels of detection related to herbicide usage as reported by USDA-NASS (Coupe et al., 1998).

Understanding the implications of BMPs on surface water contamination is key to improving water quality, especially as most of the major drainage systems in Mississippi eventually drain into the Mississippi River. For example, studies conducted at Baton Rouge, Louisiana (Clark and Goolsby, 2000) indicated that the herbicides atrazine, cyanazine and metolachlor are being discharged into the Gulf of Mexico via the Mississippi River. Although most of this is attributed to herbicide usage in the upper Midwest, potential contributions from agricultural activities in the Mississippi Delta area must also be minimized. Studies such as the MSEA project as described in Zablotowicz et al. (2004) provide a basis for understanding how implementation of BMPs can minimize contamination and improve water quality. This paper differs from that of Zablotowicz et al. (2004) in that it evaluates lake water quality after some of the BMPs were removed and land use and management practices changed.

2. Methods

2.1. Watershed descriptions and land use

Three small oxbow lake watersheds located in the central Mississippi Delta were selected as study areas. Physical characteristics and land management practices are summarized in Table 1, and cropping patterns are summarized in Table 2. Crop management and herbicide application data were collected by the Project Manager

Table 1
Physical characteristics of the three oxbow watersheds and land management practices utilized

Land use	Watershed		
	Beasley	Deep Hollow	Thighman
Total area of watershed	850 ha	202 ha	1497 ha
Forest	323 ha	124	81
Lake area	25 ha	8 ha	8.9 ha
Land/lake ratio	34	25	254
County	Sunflower	LeFlore	Sunflower
Tillage	CT until 2001, RT thereafter	NT until 2001, CT thereafter	Mostly CT, some reduced tillage
Edge of field practices	Vegetative Filter strips, slotted board inlet pipes and risers	Vegetative Filter strips, slotted board inlet pipes and risers	Overfall pipes and pads installed in 2001 and 2002

CT = conventional tillage, RT = reduced tillage, NT = no tillage.

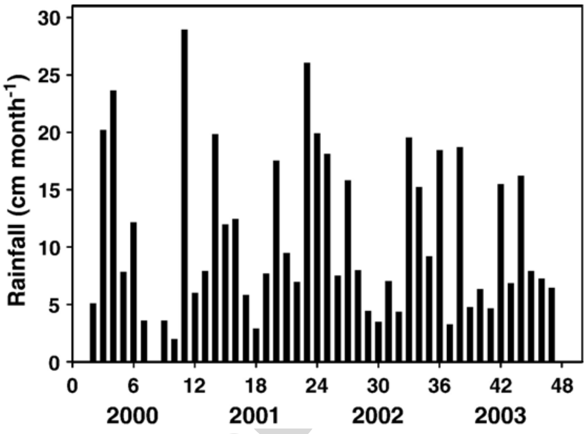

Fig. 1. Monthly rainfall observed at the Thighman Lake weather station, data summarized from information accessed from Mississippi State Experiment Station website.

(Gwin, unpublished). Monthly rainfall data for Thighman Lake (Fig. 1) was obtained from Mississippi State Experiment Station (2005) Weather Station.

Thighman Lake watershed south of Moorehead in Sunflower County is the largest watershed with a drainage area of 1497 ha, and the surface area of the oxbow lake is 8.9 ha. Thus, runoff would be concentrated into a fairly small water body. However, unlike the other two watersheds, this lake is not a closed system in that there is a constant outflow of water into a creek at the southernmost point on the lake. This watershed is the most diverse in terms of agricultural use and is managed by several farmers. Originally cotton was the dominant crop, however, after 2000, less than 14% of the arable land was under cotton production. About 6% of the watershed is used for catfish production, and less than 5% of the watershed is forested. Thighman watershed was originally established as the control MSEA watershed with traditional farming practices and no BMPs established by the project. However, towards the end of the study period, most of the farmers had adopted some degree of conservation management practice. During 2001 and 2002, structural BMPs such as graded pipes and pads were installed in strategic locations throughout Thighman watershed.

Table 2
Agricultural land use of arable land in the three oxbow watersheds

Watershed	Crop	Agricultural use of the watersheds (% of total area)			
		2000	2001	2002	2003
Thighman	Catfish	5.4	5.4	5.4	5.4
Beasley	Corn	3.7	0	0	0
D. Hollow	Corn	0	0	0	0
Thighman	Corn	21.8	22.2	9.1	18.1
Beasley	Cotton	82.4	92.0 (RR)[a]	18.1 (RR)	9.7 (RR)
D. Hollow	Cotton	21.4	21.4	21.4	21.4 (RR)
Thighman	Cotton	1.0	12.0 (RR)	7.6 (RR)	0
Thighman	Rice	1.5	4.3	7.8	9.9
Beasley	Sorghum	0	4.0	10.3	6.8
D. Hollow	Sorghum	0	0	0	0
Thigman	Sorghum	10.9	0.8	0	0.1
Beasley	Soybean	15.2	2.8	51.3 (RR)	42.2 (RR)
D. Hollow	Soybean	25.4 (RR)	25.4 (RR)	25.4 (RR)	25.4 (RR)
Thighman	Soybean	33.4 (RR)	14.9 (RR)	40.5 (RR)	18.1 (RR)
Beasley	Wheat	0	0	8.9	0
Thighman	Wheat	0	16.8	7.5	0

[a] Glyphosate-resistant cotton or soybean planted.

Beasley Lake watershed located south of Indianola in Sunflower County has a drainage area of 850 ha and is the largest of the oxbow lakes (25 ha). The Sunflower River delineates Beasley watershed on the northern edge, and during periods of high lake stage, overflow is directed into the Sunflower River. Approximately 38% of this watershed is wooded, and there is a large forested riparian zone on the eastern edge of the lake. Beasley watershed was cropped predominantly in cotton and soybeans for most of the study period with limited acreage in corn and sorghum (Table 2). For purposes of the MSEA project, Beasley Lake watershed was designated to contain only structural and vegetative edge-of-field BMPs. The structural BMPs included graded pipes with slotted board risers or slotted inlets, and vegetative filter strips were established along the lake or in turn-rows. The cropped area was maintained under conventional tillage until the spring of 2001, when glyphosate-resistant cotton and soybean facilitated the implementation of conservation management in portions of the watershed.

Deep Hollow located near Sidon in Leflore County is the smallest watershed (drainage area of 202 ha), and contains an oxbow lake with a surface area of 8.1 ha. The watershed is bordered by the Yazoo River on the west and has a large forested riparian zone bordering the western side of the lake. During periods of high precipitation, some runoff from this watershed may flow into the Yazoo River. Periodically, the Yazoo River overflows and floods the watershed. For the MSEA Project, both edge-of-field (structural and vegetative) and agronomic BMP's were implemented in Deep Hollow watershed. Throughout the study period, cotton was planted on the medium textured soils, and soybean production was on the heavier textured soils (Table 2). Each year of the study through 1999, a winter wheat cover crop was planted on all cropped land in the Fall and was herbicide-desiccated prior to planting cotton or soybeans the following Spring. Glyphosate-resistant soybeans were grown using no-tillage management. Cotton was managed under reduced tillage (subsoiling and bed formation in the fall) from 1994 to 2000. From the spring of 2000 until the end of the study period, all cotton and soybean land was returned to conventional tillage, which included multiple tillage operations.

2.2. Water sampling and processing

Surface water samples were collected monthly from three fixed locations in each of the three oxbow lakes as described by Zablotowicz et al. (2004). Samples were refrigerated immediately and stored at 5 °C until processing, typically within 24 h. Water samples (a total of 500 mL) were centrifuged in 250-mL polypropylene centrifuge bottles (10 min, 6000×g). The supernatant was decanted into glass bottles, and the weight of residual sediment in the pellet was determined after drying at 60 °C for 48 h. The combined supernatants were acidified with 1 N HCl to a pH of 3.0 and concentrated by passing through a 1000-mg C_{18} solid phase extraction (SPE) cartridge (Varian Instruments). SPE columns were preconditioned with 18 mL of ethyl acetate, followed by 6 mL of methanol, and a final rinse with 24 mL of deionized water. Herbicides and metabolites were eluted from the SPE cartridge with 20 mL of ethyl acetate. Residual water was removed from the ethyl acetate by adding 1.0 g anhydrous sodium sulfate, and the volume was reduced to 1.0 mL under N_2 gas.

2.3. Analytical methods

Ethyl acetate extracts were analyzed for atrazine, cyanazine, de-ethyl atrazine [DEA], and metolachlor using a Varian CP-3800 Gas Chromatograph (GC) equipped with a Saturn 2000 Mass spectrophotometer (MS) MS/MS (Varian Inc., Palo Alto, CA). Gas chromatographic conditions, such as column type, temperature program, Helium flow rates, and injector type and settings were previously described (Lerch and Blanchard, 2003). The ion trap mass spectrometer was run in selective ion storage mode to provide sensitivity in the low parts per trillion range for analytes. Minimum detectable concentrations for analytes determined by GC-MS were 0.3 μg L^{-1}. Recovery of spiked herbicides and that of a surrogate tertbutylazine from water samples collected from all three lakes were about 85% or greater. The lowest recoveries were from Thighman Lake, which had the highest suspended solids.

Lower concentrations of fluometuron were observed in many samples compared to previous years (Zablotowicz et al., 2004); fluometuron concentrations in unprocessed water samples were analyzed by enzyme linked immunoabsorbant assays [ELISA] (Shankle et al., 2001) using commercial kits (EnviroLogix Inc., Portland, ME). There is a very low level of cross reactivity with the major metabolite des-methyl fluometuron or related phenyl urea herbicides (EnviroLogix Inc., Portland, ME). The minimum detection limit for ELISA is 0.05 μg L^{-1}. Confirmation of fluometuron in ethyl acetate extracts was conducted using HPLC as described elsewhere (Zablotowicz et al., 2004). Since we observed that fluometuron was subject to thermal degradation to trifluromethyl aniline (Locke, 1993), we were unable to quantify fluometuron using GC-MS.

3. Results and discussion

3.1. Suspended solids and rainfall distribution

Concentrations of suspended solids observed in water samples during the study period are presented in Fig. 2. Overall, levels of suspended solids found in Deep Hollow Lake remained relatively low throughout the study period, whereas suspended solid levels in Beasley Lake decreased over the last 2 years of the study. Thighman Lake (control watershed) had the least BMP practices imposed, and it maintained comparatively high suspended solids throughout the study. Apparently installation of overflow pipes on most critical fields during 2001 and 2002 had limited effect on sediment load into Thighman Lake. A change from conventional to reduced tillage in much of Beasley watershed reduced suspended solids in Beasley Lake. Reverting the cotton land in Deep Hollow watershed to conventional tillage, however, had little influence on levels of suspended solids of water from Deep Hollow

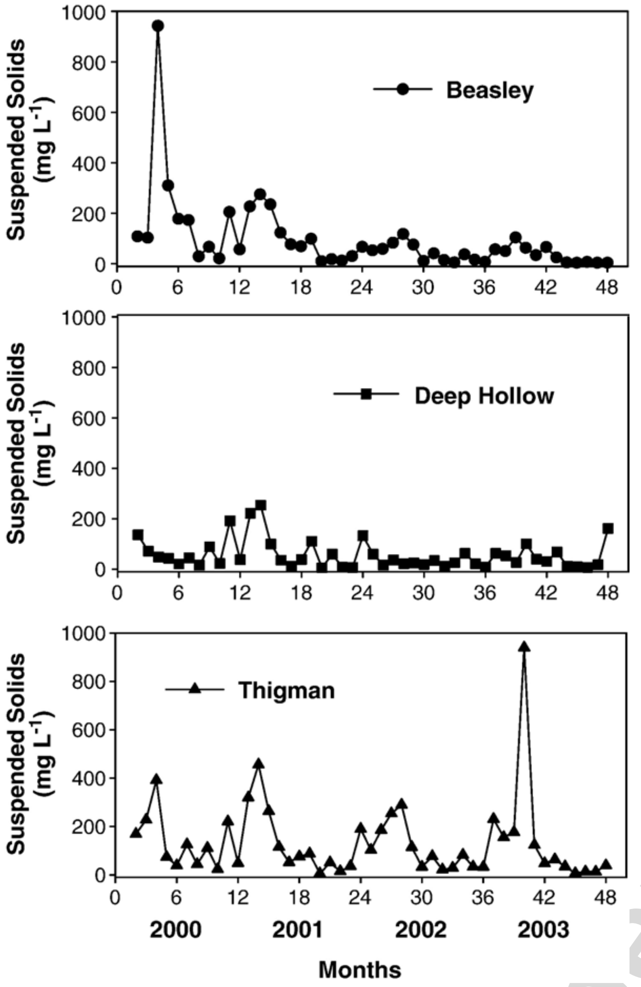

Fig. 2. Mean monthly suspended solids observed in MD-MSEA lakes in 2000 to 2003, each point represents a mean of three replicates.

Lake. The highest levels of suspended solids were found during the winter and early spring which generally coincided with the highest rainfall (data presented for Thighman Lake, Fig. 1). In 2000, 2001, and 2002 there was comparatively lower rainfall in the summer months, while in 2003, most of the Mississippi Delta received abundant summer precipitation.

3.2. Maximum herbicide concentrations

A summary of detections for the five major herbicides is presented in Table 3. Overall the highest concentrations of atrazine, the metabolite de-ethyl atrazine, and metolachlor were observed in Thighman Lake, while the highest concentrations of pesticides associated with conventional cotton production were observed in Deep Hollow Lake. In 2000, the maximum concentrations of fluometuron and other herbicides were similar to that reported in other studies in the Southern United States (Senseman et al., 1997; Thurman et al., 1998, 2000). Generally, many herbicides follow the pattern of maximum concentrations observed in the spring flush shortly after the first rainfall events following herbicide applications (Thurman et al., 1991). Overall, the change in occurrence of herbicides in these Mississippi Delta watersheds is likely due to changes in cropping patterns and herbicide use, as seen in Midwestern United States streams (Scribner et al., 2000).

3.3. Cotton herbicides

The phenyl urea cotton herbicide, fluometuron, was observed in all three lakes in 2000 (Fig. 3), with the

Table 3
Maximum herbicide concentrations and frequency of detections observed in three MSEA oxbow lakes, 2000 to 2003

	Concentration ($\mu g\ L^{-1}$)			
	2000	2001	2002	2003
Atrazine				
Beasley	2.30 (May) 31/33	0.84 (May) 20/36	2.74 (April) 15/36	0.36 (May) 27/36
Deep Hollow	0.15 (April) 11/33	0.05 (Oct.) 4/36	0.18 (April) 7/36	<0.03 0/36
Thighman	23.4 (May) 33/33	11.7 (April) 19/36	7.1 (April) 27/36	21.8 (April) 36/36
Cyanazine				
Beasley	1.62 (Aug.) 28/33	0.34 (July) 7/36	<0.03 0/36	<0.03 0/36
Deep Hollow	5.48 (Aug.) 33/33	0.33 (July) 9/36	0.24 (July) 9/36	<0.03 0/36
Thighman	0.50 (March) 30/33	<0.03 0/36	<0.03 0/36	<0.03 0/36
De-ethyl atrazine				
Beasley	0.77 (Sept.) 31/33	0.16 (July) 10/36	0.08 (July) 3/36	0.26 (July) 6/36
Deep Hollow	0.23 12/33	0.09 1/36	<0.03 0/36	<0.03 0/36
Thighman	2.00 (July) 30/33	0.38 (June) 11/36	0.69 (April) 15/36	0.49 (April) 9/36
Fluometuron				
Beasley	2.87 (June) 33/33	0.10 (March) 3/36	0.21 (Aug.) 2/36	<0.05 0/36
Deep Hollow	0.85 (June) 30/33	1.96 (June) 30/36	2.47 (June) 36/36	0.12 (Feb.) 5/36
Thighman	2.02 (June) 27/33	0.09 (March) 3/36	0.07 (July) 1/36	<0.05 0/36
Metolachlor				
Beasley	0.47 (May) 30/33	1.60 (July) 31/33	0.29 (June) 30/33	0.30 (May) 28/33
Deep Hollow	0.42 (July) 3/33	0.20 (May) 14/36	0.17 (April) 6/36	<0.03 0/36
Thighman	14.9 (May) 29/33	6.0 (April) 36/36	0.66 (May) 11/36	4.8 (April) 13/36

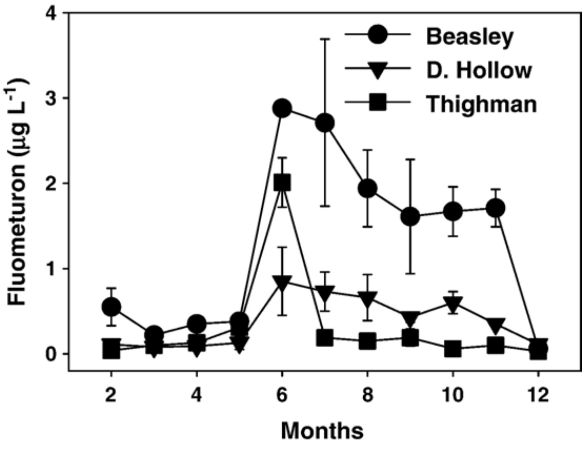

Fig. 3. Mean monthly fluometuron concentrations observed in MD-MSEA lakes in 2000, mean and standard deviation of three replicates.

highest levels found in Beasley Lake. However, during the remainder of the study, fluometuron was detected only in Deep Hollow Lake (Table 3, Fig. 4). In 2000, fluometuron levels remained relatively high in Beasley Lake from June until November, and rapidly declined. Fluometuron occurrence in Thighman Lake was limited to a single pulse in June, the maximum concentration detected in 2000 was at least ten-fold less than observed in 1996 through 1998 when less conservation management was utilized, and more cotton was planted in Thighman Watershed (Zablotowicz et al., 2004). A transition from conventional herbicide regime to a glyphosate-resistant cropping system was largely responsible for a reduction in fluometuron detections in Beasley and Thighman watersheds during 2001 to 2003 (Table 2). This is in agreement to statewide surveys on herbicide usage in cotton (USDA-NASS).

Cotton is typically planted in May, and peak fluometuron concentrations in Deep Hollow Lake were generally observed after the first major rainfall event after planting. Although there was only a minor increase in suspended solids in water in Deep Hollow Lake, fluometuron concentrations increased about three-fold from 2000 to 2002 suggesting that it was predominantly transported in the dissolved phase. In a Georgia field study reported by Potter et al. (2004), fluometuron transport in runoff was shown to occur primarily in the dissolved phase and not bound to sediments. This was attributed to its relative water solubility. Locke et al. (2005) observed that during the 30-day period following herbicide application to a Mississippi Delta soil similar to those in Deep Hollow Lake watershed, fluometuron concentrations in the surface of conventional or no-tillage soils were typically 66% greater than in lower depths (below 2 cm), where herbicide is less vulnerable to loss in runoff. Given the relative water solubility of fluometuron and the close proximity to time of herbicide application in the current Deep Hollow Lake study, higher concentrations in lake water might be expected.

In Deep Hollow Lake, fluometuron levels increased incrementally from 2000 to 2002. This change corresponded to the period when tillage practice shifted from conservation management (reduced tillage and a wheat winter cover crop) to conventional tillage with no cover crop (Fig. 4). Several studies in the literature have demonstrated a lower loss of pesticides in runoff under reduced tillage systems (Hall et al., 1991; Miao et al., 2004; Richards et al., 2002). Similarly, for fluometuron in particular, Potter et al. (2004) measured greater runoff loss of fluometuron from sandy Georgia soils under conventional tillage, compared to strip tillage under natural rainfall conditions. In Mississippi field studies, Baughman et al. (2001) observed 19% more fluometuron and 305% greater sediment loss in runoff from conventionally tilled plots compared to no-tillage plots with a rye grass cover. Locke et al. (2005) found that ryegrass and rye cover crop residues under no-tillage cotton intercepted a majority of applied fluometuron and impeded subsequent movement into soil. The present study at Deep Hollow therefore provides a watershed scale perspective as to the potential effects of converting a soil that has been under continuous conservation tillage for 6 years to conventional tillage with regard to the potential for loss of herbicides to surface water.

Before it was withdrawn from the market in 2000 (USEPA, 2000), the triazine herbicide cyanazine was widely used as a late season application in cotton in the Mississippi Delta. In August of 2000, levels of cyanazine found in Deep Hollow were about three-fold greater than those found in Beasley (Table 3, Fig. 5). In contrast, the highest levels of cyanazine found in Thighman Lake

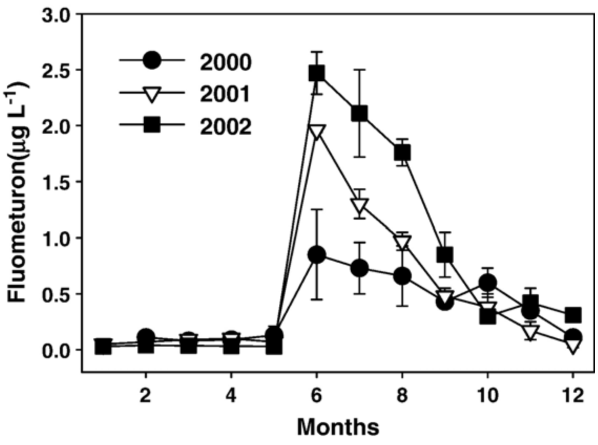

Fig. 4. Mean monthly fluometuron concentrations in Deep Hollow Lake in 2000 to 2002, mean and standard deviation of three replicates.

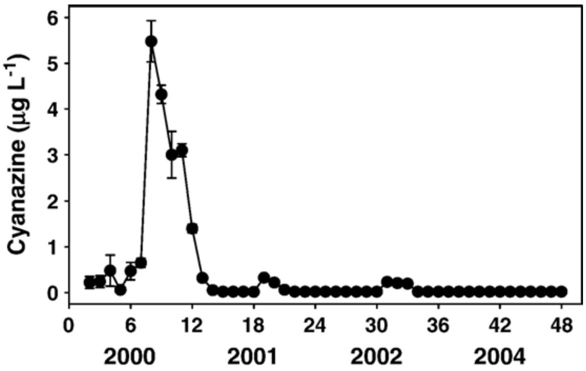

Fig. 5. Mean cyanazine concentrations, Deep Hollow Lake, mean and standard deviation of three replicates, if not shown standard deviation is less than symbol size.

(0.5 μg L^{-1}) occurred in March of 2000 (Table 3), suggesting that these observations were associated with corn and not cotton usage. Lower concentrations (<0.4 μg L^{-1}) were observed in Beasley and Deep Hollow in 2001, while cyanazine was only found in Deep Hollow Lake (0.26 μg L^{-1}) in 2002. Cyanazine concentrations observed in Beasley Lake in 2001 were about 20% of that in 2002, corresponding to application on 2.8% of the watershed in 2001 compared to 15.2% in 2000. No cyanazine was detected in any lake in 2003. The levels of cyanazine found in Deep Hollow Lake were about four-fold greater than previously reported for 1998 (Zablotowicz et al., 2004), although similar application rates were used on the same amount of cotton area. In 2000 the U.S. EPA cancelled the registration of cyanazine under the provision of no further sales after September 1999, with allowance of continued use only until December 2002 (USEPA, 2000). The pattern of decreasing cyanazine levels observed in water from these watersheds indicates compliance with these regulations.

3.4. Corn herbicides

The occurrences of atrazine, de-ethyl atrazine, and metolachlor were associated with the amount of corn and/or sorghum planted in the watershed, and were typically observed in Beasley and Thighman Lake water samples (Table 3), but rarely detected in Deep Hollow. Although higher levels of atrazine were detected in Thighman Lake, the pattern of occurrence in this lake was typically as a single peak within a month of corn planting (Fig. 6a). By contrast maximum concentrations of atrazine detected in Beasley Lake were about 10-fold less than Thighman Lake, however relative concentrations remained higher for several months after planting of corn (Fig. 6b). The atrazine metabolite DEA, when detected in Thighman Lake, was typically less than 10% of the maximum concentration of atrazine observed (Table 3), while the highest DEA concentration observed in Beasley Lake was about 72% of the maximum atrazine concentration for this lake in 2003. De-isopropyl atrazine was detected in less than 10% of the water samples from Beasley or Thighman Lake and its maximum concentration was about 25% of DEA (data not shown). In the 4 years about 15% of the water samples collected from Deep Hollow Lake contained a low level of atrazine (<0.15 μg L^{-1}), although there was no corn planted or atrazine used on this watershed. Deep Hollow watershed is adjacent to the Yazoo River, and it is possible that there was some flow from this river into the oxbow lake. Earlier studies by Coupe et al. (1998) in three Mississippi Delta streams indicated a low occurrence of atrazine. The pattern of atrazine occurrence in Thighman Lake indicated that most of the atrazine loss occurred from runoff events immediately following planting. The higher concentrations found at Thighman Lake were indicative of runoff from a larger area of application being accumulated into a small water body, consistent with higher land to lake ratios (Table 1). The levels of atrazine detected in Beasley and Thighman Lake were similar to those observed in surface waters in

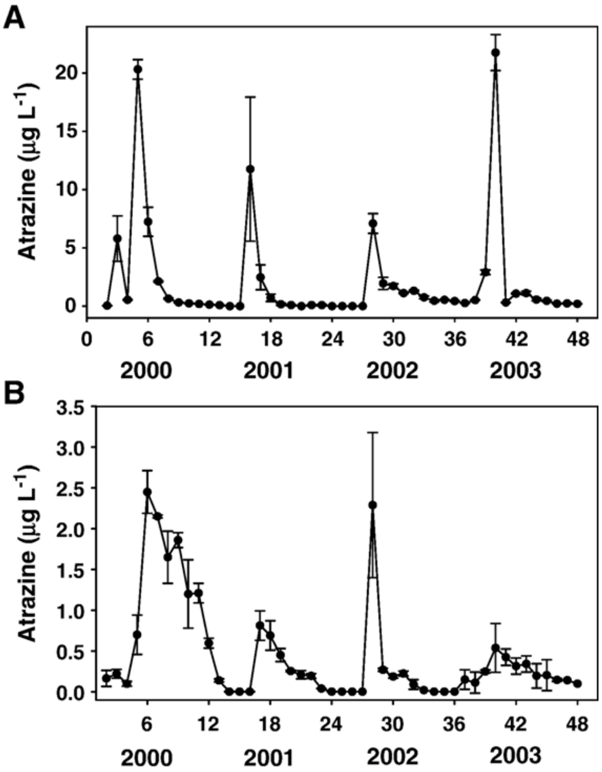

Fig. 6. Mean atrazine concentrations in Thighman Lake (A) and Beasley Lake (B), each point represents a mean and standard deviation of three replicates, if not shown standard deviation is less than symbol size.

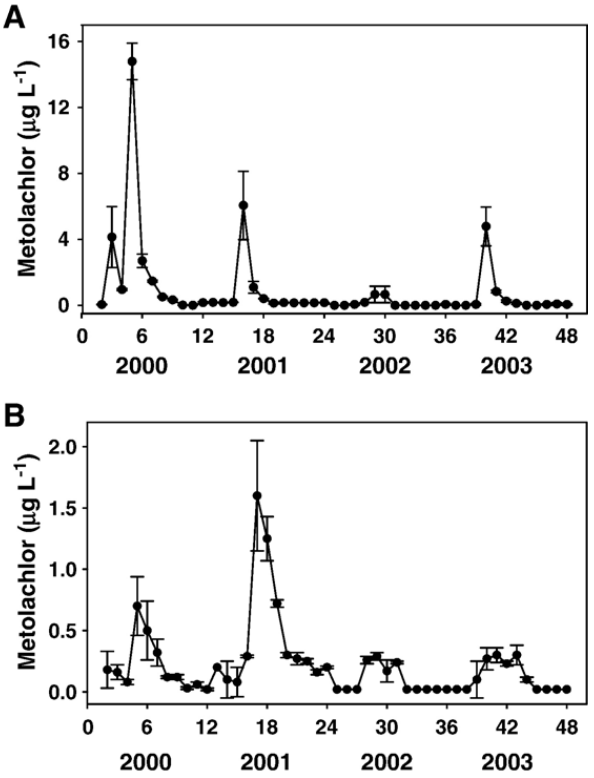

Fig. 7. Mean metolachlor concentrations in Thighman Lake (A) and Beasley Lake (B), each point represents a mean and standard deviation of three replicates, if not shown standard deviation is less than symbol size.

the Midwestern United States (Jaynes et al., 1999; Goolsby and Battaglin, 1995; Lerch and Blanchard, 2003; Scribner et al., 2000; Thurman et al., 1991). These present studies indicate that under conventional corn production, peak concentrations of atrazine attain a level considered to have adverse toxicological implications to aquatic health (Solomon et al., 1969). During the study period, a few producers adopted glyphosate-resistant corn; it is anticipated that there should be continued interest in the occurrence of atrazine in surface water of the Mississippi Delta.

Patterns of metolachlor concentration in Thighman Lake were similar to those observed for atrazine concentrations, e.g., maximum concentration in April, typically occurring as a narrow pulse (Fig. 7a). However, after 2000, relatively lower concentrations of metolachlor were observed compared to atrazine in Thighman Lake. The maximum metolachlor concentrations detected in 2001 to 2003 were less than one third of the maximum concentration observed in 2000. In Beasley Lake watershed, *s*-metolachlor was applied at planting in the corn, cotton and sorghum during this study period. The highest concentrations of metolachlor found in Beasley Lake in 2001 were about twice as high as those found in 2000, even though metolachlor was applied at a similar rate to equal acreage in 2000 and 2001. In 2002 and 2003 metolachlor was observed at lower levels (<0.30 µg L^{-1}) in Beasley Lake, but was applied only to the land under sorghum production. Decreased levels of metolachlor were most likely due to a change in use of *s*-metolachlor (Dual Magnum) versus the enantiomeric mixture of metolachlor that was previously marketed until 1999, and increased use of glyphosate-resistant crops. In 2000, most of the growers in Thighman watershed still used the conventional mixture, using the *s*-metolachlor thereafter. The *s*-form of metolachlor has greater herbicidal activity (O'Connell et al., 1998) and application rates can be reduced to about 35% of that of the metolachlor mixture with no loss in weed control efficacy.

4. Conclusion

These data indicate that in the three watersheds studied there was a general trend for a reduction in the level of herbicides detected. Most of this can be explained by a shift to the use of glyphosate-resistant cotton and soybeans. Although significant changes in land management occurred during the study period, the impacts of altering tillage management on herbicide runoff were difficult to assess, except in the case of fluometuron in Deep Hollow watershed. These studies provide additional background on the degrees of herbicide persistence in water of small oxbow lakes that may prove useful in ecotoxicological assessments of water quality in the Mississippi Delta.

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