



Distribution and Spatial Variation in Surface Sediment Pesticides of Mississippi Alluvial Plain

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Abstract: As part of a broader sediment quality assessment, we examined the effects of varying land-use practices on sediment pesticide contamination in water bodies within the lower Mississippi alluvial plain (LMAP), USA. Three categories of land-use practices were studied: intensive row-crop agriculture (water bodies listed as impaired according to USEPA section 303d Clean Water Act), row-crop treated with best management practices (BMP), and <1% row crop within White River National Wildlife Refuge (NWR). Seventeen current and historic-use pesticides were measured in surface sediments (top 5 cm) within three 303d, BMP and NWR water bodies (nine total) from June-July 2004. Significant ($P < 0.05$) spatial variation occurred in 10 of 17 pesticides measured in sediments. Current-use herbicides were greatest in 2 of 3 NWR water body sediments and lowest in 2 of 3 BMP water body sediments. Current-use insecticides were greatest in 2 of 3 NWR water body sediments but lowest in 303d sediments. In contrast, historic-use pesticides (ΣDDT) were greater in 303d sediments and lower in BMP sediments. Columbus Lake (NWR) sediment had consistently lower concentrations for nearly all pesticides. Overall spatial patterns of sediment pesticide contamination in LMAP were due to agricultural land-use practices as well as the degree of static or flow-through conditions of each water body. Results indicate that while NWR water bodies have extensive natural riparian areas that can process contaminants, they still receive significant influx of current-use pesticides, and BMPs treating similar water bodies can mitigate the degree of sediment contamination.

Key words: Agriculture, Sediment quality, Insecticide, Herbicide, Best Management Practices.

Introduction

Pesticide use is an integral and essential part of modern agriculture especially in the Lower Mississippi Alluvial Plain also referred to as the Mississippi Delta. Agriculture has become increasingly dependent upon pesticides escalating their use by 60% between 1964 and 1990 (World Resource Institute 1992). Although pesticides used to control detrimental weeds and insects have changed since the wide spread use of highly persistent organochlorine insecticides in the 1940's through the 1970's, pesticides still present environmental problems. Use of most persistent pesticides was curtailed in the 1970's, however 30 years of widespread use resulted in world-wide contamination in both biotic and abiotic components of terrestrial and aquatic ecosystems (Woodwell et al. 1971; Crump-Wiesner et al. 1974). Persistent insecticides continue to be reported as low-level contaminants in aquatic ecosystems in the lower Mississippi River alluvial plain (Cooper et al. 1987; Cooper and Knight 1987).

Extent and concentration of contamination by pesticides depend on several factors including the specific combination of chemicals, soil characteristics, management practices, and

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climatic variables (Rao and Jessup 1983; Helling and Gish 1986; Cheng and Koskinen 1986; Jury et al. 1987; Seiber 1987; Leonard and Knisel 1988; McBride et al. 1988). Smith et al. (2001) attributed contaminants associated and transported with sediments as the likely the source of pyrethroids in shallow ground water in Mississippi Delta oxbow watersheds. Since such factors as flow path length from source to receiving water and the residence time and decomposition rate affect the concentration of agrichemicals (Moody 1990) agricultural management practices that slow runoff, trap sediments and enhance agrichemical processing and retention may contribute significantly in the reduction of pesticide contamination. These practices include conservation tillage, grass filter strips, stiff grass hedges, grassed waterways, slotted board riser pipes, and agricultural ditches.

In the United States, national laws such as the Clean Water Act recognize specific agricultural practices known as “Best Management Practices” (BMPs) as those preferred methods to reduce nonpoint source pollution. BMPs are typically implemented on farms on a voluntary basis with funding provided through cost-share programs if available. While these “Best Management Practices” have been tested for their effectiveness in reducing agricultural related pollutants on test plot scales, they typically have not been evaluated on a farm watershed scale nor have they been evaluated in terms of their impact on downstream ecology. Determining the ability of best management practices (BMPs) in mitigating pesticide contamination of sediment is an important part of understanding the extent of overall potential contamination in delta watersheds. The purpose of the present study was to examine and compare patterns in concentrations of 12 current-use pesticides, two historic-use pesticides and 3 metabolites during summer 2004 in surface sediments from three land-use category water bodies, reference, BMP, and impaired (according to USEPA section 303d Clean Water Act).

Materials and Method

Study Site Description

Selected study sites were located in the states of Arkansas and Mississippi, USA, within the lower Mississippi alluvial plain (LMAP) (Figure 1). Nine water bodies were divided into three land-use categories within their respective watersheds as follows: intensive row-crop agriculture, listed as impaired according to USEPA section 303d Clean Water Act (303d) (MDEQ 2004); intensive row-crop agriculture treated with best management practices (BMP) described by Locke et al. (2004); and less than 1% row-crop agriculture within the White River National Wildlife Refuge (NWR) (USFWS 2006). BMP treated water bodies include Beasley Lake located in Sunflower County, Mississippi, Deep Hollow Lake located in Leflore County, Mississippi, and Thighman Lake located in Sunflower County, Mississippi. NWR water bodies comprised Columbus Lake located in Arkansas County, Arkansas, Lower White Lake located in Arkansas County, Arkansas, and Upper Swan Lake located in Monroe County, Arkansas. Impaired 303d water bodies comprised Bee Lake located in Holmes County, Mississippi, Cassidy Bayou located in Tallahatchie County, Mississippi, and Roebuck Lake located in Leflore County, Mississippi. Three sites were selected longitudinally within each of the nine water bodies for a total of 27 sampling sites.

Sample Collection

Surface sediment samples were collected within a five week period either during or shortly following peak seasonal herbicide and insecticide recommended application periods. BMP sediment samples were collected on June 17, 2004, 303d sediment samples were collected on July 8, 2004, and NWR sediment samples were collected on July 22, 2004. At each of the 27 sampling sites, two 1 L surface sediment samples (5 cm depth) were collected with an acetone rinsed Ekman dredge sampler (modified from Cooper et al. 2003). Sediment was transferred to acetone/hexane triple washed amber colored glass jars fitted with a Teflon[®]-lined, screw cap using an acetone washed stainless steel trowel, preserved on ice and transported to the USDA-ARS National Sedimentation Laboratory, Oxford, MS for preparation and analysis. Sample preparation ensued within 24 h of collection. Dried sediments were ground and 15 g was sub-

sampled for extraction using distilled reagent grade ethyl acetate prior to analysis (modified from Bennett et al. 2000).

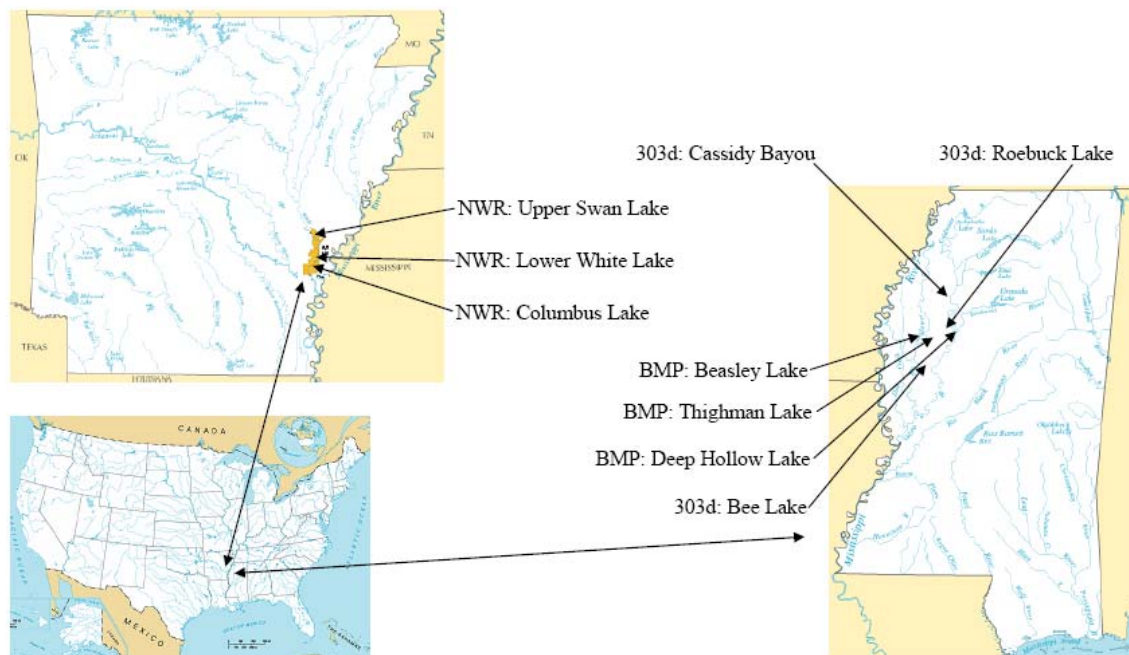


Figure 1. Location of the White River National Wildlife Refuge water bodies (NWR), Arkansas, Best Management Practices water bodies (BMP), Mississippi, and USEPA section 303(d) Clean Water Act listed water bodies (303d), Mississippi.

Sample Preparation and Pesticide Analysis

Sediments were air dried and ground to pass a 2 mm sieve. A 15 g sub-sample was taken for pesticide analysis via a method similar to that of Bennett et al. (2000) and modified by Smith and Cooper (2004). This involved extraction with pesticide-grade ethyl acetate, silica gel column chromatography cleanup, and concentration to 1 mL volume under high purity dry nitrogen. Recoveries based on fortified samples were >89% for all pesticides (and/or metabolites). Two Hewlett Packard (now Agilent) model 6890 gas chromatographs (GCs) each equipped with dual HP 7683 ALS auto injectors, dual split-splitless inlets, dual capillary columns, an HP Kayak XA Chemstation were used to conduct all pesticide analyses (Smith and Cooper 2004). One HP 6890 was equipped with two HP micro electron capture detectors (μ ECDs) and the other 6890, with one HP μ ECD, one HP nitrogen phosphorus detector (NPD), and an HP 5973 mass selective detector (MSD). The main analytical column was an HP 5MS capillary column (30 m x 0.25 mm i.d. x 0.25 μ m film thickness). Column oven temperatures were as follows: initial at 85°C for 1 min, ramp at 25°C min⁻¹ to 190°C, hold at 190°C for 25 min, ramp at 25°C min⁻¹ to 230°C, and hold for 30 min. The carrier gas was UHP helium at 28 cm sec⁻¹ average velocity with the inlet pressure at 8.64 psi and inlet temperature at 250°C. The μ ECD temperature was 325°C with a constant make up gas flow of 40 ml min⁻¹ UHP nitrogen. The autoinjector was set at 1.0- μ L injection volume in the fast mode. Under these GC conditions, all 17 pesticides (and/or metabolites) were analyzed in a single run of 61.80 min. When deemed necessary, pesticide residues were confirmed with an HP 1MS capillary column (30 m x .25 mm i.d. x 0.25- μ m film thickness) and/or with the MSD. The MSD was used only when there was a question as to the identity of a particular pesticide. Online HP Pesticide and NIST search libraries were used when needed. Thus we determined the sediment concentrations of six current-use herbicides and six current-use insecticides, two historic-use pesticides, pp'-DDT and dieldrin, and three metabolites, fipronil sulfone, pp'-DDD and pp'-DDE. The limit of

detection (LOD) and limit of quantitation (LOQ) for the targeted compounds is shown in Table 1.

Table 1. GC retention times, LODs, and LOQs for the targeted pesticides (and/or metabolites).

Pesticide (or metabolite)	Retention time (min)	LOD (ng kg ⁻¹)	LOQ (ng kg ⁻¹)
Trifluralin	10.63	0.1	1
Atrazine	12.31	1	10
Methyl parathion	16.78	1	10
Alachlor	17.35	0.5	5
Metolachlor	20.68	1	10
Cyanazine	20.96	0.1	1
Chlorpyrifos	21.17	0.1	1
Pendimethalin	25.06	0.5	5
Fipronil	26.78	0.1	1
<i>p,p'</i> -DDE	32.17	0.1	1
Dieldrin	32.29	0.1	1
Fipronil sulfone	33.28	0.1	1
Chlorfenapyr	34.13	0.5	5
<i>p,p'</i> -DDD	34.95	1	10
<i>p,p'</i> -DDT	37.70	1	10
Bifenthrin	43.36	0.1	1
λ -Cyhalothrin	51.01	0.1	1

Data Analysis

Spatial variation of surface sediment pesticide concentrations was assessed using descriptive statistics to calculate median values and 25 and 75 percentiles for each water body (N = 6). Tests for normality, using the Kolmogorov-Smirnov test, and homoscedasticity (equal variance), using the Levene Median test (Steel et al. 1997), were conducted with results failing to meet parametric assumptions. Because of this a Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks was performed with probability (*P*) set at the 5% significance level. When median values were significantly different, a Student-Newman-Keuls (SNK) multiple range test was employed to compare differences of median pesticide concentrations across water bodies (Steel et al. 1997). Data analysis was performed using SigmaStat® v.2.03 statistical software (SPSS 1997).

Results

Surface sediment contamination within the lower Mississippi alluvial plain was widespread and occurred even in samples from water bodies in watersheds with <1% row-crop land-use. Of the 54 sediment samples collected from LMAP during summer 2004, analysis of the 17 pesticide suite yielded 918 possible detections of which 545 (59%) were observed. At least one pesticide of the 17 pesticide suite was detected in every sediment sample. Sediment pesticides in row-crop land-use water bodies (303d) occurred most frequently with 201 of 306 possible detections (66%). Pesticides in BMP treated row-crop land-use water bodies were intermediate with 175 of 306 detections (57%) and pesticides in less than 1% row-crop land-use water bodies were least frequent with 168 of 306 detections (55%). While aqueous pesticide contamination in runoff, shallow ground water and surface waters occur infrequently in conjunction with applications and/or ensuing storm events (Cooper et al. 1987; Cooper 1991b; Cooper et al. 2003; Smith and Cooper 2004; Smith et al. 2006), sediment contamination is cumulative due to the nature of sediment to act as a sink for hydrophobic and less hydrophilic pesticides. This

produces chronic contamination of the water body due to the less transient aspect of pesticides actively partitioning to sediment during one or more aqueous contamination events and ensuing release via desorption or resuspension of sediment particles with sediments potentially acting as a source of pesticide contamination (Wenning et al. 2005).

The influence of varying agricultural land-use on LMAP sediment pesticide contamination was assessed in three broad groups: current-use herbicides, current-use pesticides, and historic-use pesticides and metabolites. LMAP sediment herbicide contamination was the least frequently occurring with 147 of 324 possible detections (45%). Of the six herbicides assessed across all land-use categories, atrazine (83%) and metolachlor (69%) occurred most frequently and trifluralin (19%) and pendimethalin (11%) the least frequent. In addition, atrazine, when detected, frequently occurred in concentrations greater than 100 ng g⁻¹ (22 of 45 detections) whereas metolachlor, when detected, only occasionally occurred in concentrations greater than 100 ng g⁻¹ (7 of 37 detections). Sediment herbicides in row-crop land-use water bodies (303d) occurred most frequently (51%), less than 1% row-crop land-use water bodies (NWR) were intermediate (45%) and BMP treated row-crop land-use water bodies least frequent (41%). Statistical comparisons of surface sediment herbicide concentrations examined among nine watersheds within the LMAP revealed spatial patterns. Significant variation ($P < 0.05$) occurred in median values of four of six herbicides measured in surface sediments (Table 2). Median atrazine, metolachlor and cyanazine sediment concentrations were greatest in Lower White Lake (NWR) and Upper Swan Lake (NWR) and alachlor was greatest in Bee Lake (303d). Lowest median atrazine, metolachlor and alachlor concentrations were in Beasley Lake (BMP), Cassidy Bayou (303d) and Roebuck Lake (303d), respectively. Although applications of these herbicides occurred weeks to months prior to sampling, these compounds are widely used in significant quantities with 7,413,000 kg of atrazine and 876,000 kg of metolachlor used in 2003 (USDA-NASS 2006). In addition, several have a significant affinity for sediment particles (Smith and Cooper 2004) and can be persistent in sediment for several months with atrazine and metolachlor half-lives of 60 to >100 days and 15 to 70 days, respectively (EXTOXNET 1996).

Table 2. Median (75 percentile) current-use herbicide concentrations (ng g⁻¹, dw) in sediments from nine watersheds in the Lower Mississippi Alluvial Plain during summer 2004 (ND= below detection limit for all six samples). Median concentrations with the same letter are not statistically significant among water bodies ($P > 0.05$).

Water Body	Alachl	Metolachlo	Pendimethalin	Trifluralin	Atrazine	Cyanazine
Upper Swan	0.4	76.1	0 (0) A	ND A	827.2	10.1 (54.6)
Lower White	0 (0.2)	107.1	ND A	0 (0) A	950.5	15.9 (24.3)
Columbus	0 (0.7)	9.1 (33.7)	ND A	0 (0) A	16.3	0 (0) A
Beasley	0.1	2.4 (3.6) B	0 (0) A	ND A	5.2 (18.8)	0 (0) A
Thighman	0 (2.1)	17.7 (39.6)	ND A	0 (0.1) A	122.8	4.6 (6.0) B
Deep Hollow	0 (0.1)	2.4 (5.5) B	ND A	0 (0-0) A	8.9 (64.0)	0 (0) A
Bee	1.6	36.9 (59.5)	ND A	ND A	300.9	1.5 (5.0) A
Cassidy	0 (0.3)	ND A	16.3 (39.4) A	0.7 (1.2) A	32.1	0.1 (0.6) A
Roebuck	ND A	19.7 (36.5)	ND A	ND A	184.0	2.1 (4.9) A

Few studies have examined sediment current-use herbicide contamination within the LMAP region (Shea et al. 2001; Moore et al. 2004). Observed sediment herbicide concentrations were comparable to these studies with atrazine most frequent and in greatest concentrations while dinitroaniline herbicides (pendimethalin and trifluralin) occurred infrequently. Risk of ecological impairment from observed sediment current-use herbicide concentrations in LMAP is considered low. Although atrazine concentrations occasionally

exceeded 1,000 ng/g, the compound is only slightly toxic to aquatic organisms and has a relatively high affinity for sediment making it less bioavailable (EXTOXNET 1996).

Current-use insecticide LMAP sediment contamination occurred with intermediate frequency in 155 of 324 possible detections (48%). Of the six insecticides assessed across all land-use categories, chlorfenapyr (87%) and methyl parathion (61%) occurred most frequently and chlorpyrifos (33%) and λ -cyhalothrin (13%) the least frequent. While chlorfenapyr and methyl parathion occurred frequently, concentrations were typically below 20 ng/g (2 detections each) whereas chlorpyrifos when detected, often occurred in concentrations greater than 20 ng g⁻¹ (8 of 18 detections). Insecticides in surface sediment of row-crop land-use water bodies (303d) occurred most frequently (56%), less than 1% row-crop land-use water bodies (NWR) were intermediate (47%) and BMP treated row-crop land-use water bodies least frequent (40%). Statistical comparisons of sediment insecticides examined among nine watersheds within the LMAP showed spatial variation (Table 3). Median insecticide concentrations varied significantly ($P < 0.05$) in only two of six compounds, fipronil and chlorfenapyr. Chlorfenapyr was issued a FIFRA Section 18 Pesticide Emergency Exemption from 1995 to 1998 to be used on mites infesting cotton crops in LMAP and, as a result, has not been used since (USEPA OPP 2000). All observed sediment chlorfenapyr concentrations are based upon 1998 applications when 9,450 kg was applied throughout the US cotton belt (USDA NASS 2006). Greatest chlorfenapyr sediment concentrations occurred in Lower White Lake (NWR) and Upper Swan Lake (NWR) whereas lowest concentrations were in Columbus Lake (NWR) and Cassidy Bayou (NWR). Median fipronil sediment concentrations were greatest in Lower White Lake (NWR), Upper Swan Lake (NWR) and Bee Lake (303d). Lowest fipronil concentrations were Columbus Lake (NWR) where the compound was not detected. Fipronil is a pyrazole class insecticide frequently used on corn crops in April and May but also has applications for rice production. Fipronil is widely used with approximately 22,000 kg applied to corn crops in the United States during 2003 (USDA NASS 2006). Greater fipronil concentrations in sediments from NWR are associated with greater combined corn and crop production in these areas.

Table 3. Median (75 percentile) current-use insecticide concentrations (ng g⁻¹, dw) in sediments from nine watersheds in the Lower Mississippi Alluvial Plain during summer 2004 (ND= below detection limit for all six samples). Median concentrations with the same letter are not statistically significant among water bodies ($P > 0.05$).

Water	Chlorpyrifos	Methyl	λ -	Bifenthrin	Fipronil	Chlorfenapyr
Upper	0 (0) A	3.1 (6.8)	0 (11.5) A	1.3 (3.7) A	1.2 (2.0)	3.3 (10.7) C
Lower	ND A	3.3 (6.6)	0 (0) A	1.6 (2.3) A	1.1 (1.3)	4.1 (8.5) C
Columbus	12.3 (27.3)	0 (4.3) A	ND A	ND A	ND A	0 (0.3) A
Beasley	0 (8.2) A	12.6	0.6 (1.4) A	ND A	0 (0) A	0.7 (1.5) B
Thighman	12.4 (34.3)	0 (0) A	ND A	0 (0) A	0 (0) A	1.1 (1.4) B
Deep	0 (6.9) A	12.4	0 (0) A	ND A	0 (0.8) A	0.6 (0.8) B
Bee	6.7 (17.8) A	5.8 (6.1)	ND A	0.5 (2.0) A	0.7 (1.0)	1.3 (5.5) B
Cassidy	0 (0) A	6.5 (13.3)	ND A	0.4 (2.7) A	0.6 (0.8)	0.1 (0.2) A
Roebuck	0 (11.1) A	5.6 (6.9)	ND A	0.6 (1.4) A	0.4 (0.8)	0.6 (1.0) B

In the 2002 agricultural census, Arkansas and Monroe counties, Arkansas together had 10,681 ha and 70,392 ha corn and rice planted respectively, whereas Sunflower, Leflore, Holmes and Tallahatchie counties, Mississippi together had 36,217 ha and 28,086 ha corn and rice planted, respectively (USDA NASS 2006). Previous reports of current-use insecticide sediment contamination in LMAP is limited (Cooper 1991b; Shea et al. 2001; Moore et al. 2004) due to the transient nature of these compounds. These reports primarily focused on organophosphates

and pyrethroids because of their common, wide spread use in the region (USDA NASS 2006), low water solubility and high affinity for sediment (Bennett et al. 2000; Smith and Cooper 2004). The current study had comparable levels of organophosphates and pyrethroids within LMAP where organophosphates were more frequent and in greater concentrations than pyrethroids in association with recommended application rates. Risks of ecological impairment from sediment current-use insecticide concentrations in LMAP are considered low. Greatest potential for ecological impairment would be from organophosphates (e.g., methyl parathion) and pyrethroids (bifenthrin and λ -cyhalothrin) (EXTOXNET 1996).

Pyrethroid concentrations, when detected, occasionally exceeded reported effects concentrations (Amweg et al. 2005), however sediment characteristics such as total organic carbon content and sediment particle size have a significant influence on the bioavailability of these compounds (Maund et al. 1998).

Sediment contamination via historic-use insecticides and metabolites in LMAP unequivocally occurred with greatest frequency in 225 of 270 possible detections (83%). Occurrence of the two historic-use insecticides and three metabolites assessed (Table 4) across all land-use categories showed pp'-DDE (96%), pp'-DDD (93%) and pp'-DDT (93%) occurred most frequently while fipronil sulfone (52%) was least frequent. The historic-use insecticide pp'-DDT was often observed in concentrations greater than 10 ng g⁻¹ and its metabolites, pp'-DDD and pp'-DDE frequently had concentrations greater than 1 ng g⁻¹ in LMAP sediments. In contrast, dieldrin rarely exceeded 0.5 ng g⁻¹, occurring in only five samples. Historic-use insecticides and metabolites in surface sediment of BMP treated row-crop land-use water bodies and row-crop land-use water bodies (303d) occurred most frequently (98% and 96%, respectively) and less than 1% row-crop land-use water bodies (NWR) were least frequent (76%). Sediment from 303d and BMP water bodies had measurable amounts of pp'-DDT, pp'-DDD, and pp'-DDE in every sample. Significant ($P < 0.05$) spatial variation occurred in the metabolite fipronil sulfone and pp'-DDT and its metabolites (Table 4). Median fipronil sulfone concentrations were greatest in Upper Swan Lake (NWR) and lowest in Columbus Lake (NWR). Greatest median pp'-DDT occurred in Lower White Lake (NWR) and Cassidy Bayou (303d), greatest median pp'-DDD occurred in Cassidy Bayou, and greatest median pp'-DDE occurred in Cassidy Bayou and Bee Lake (303d). Columbus Lake (NWR) had the lowest median concentrations for pp'-DDT and its metabolites. Despite pp'-DDT and dieldrin being banned from use in the United States since 1972 and 1987, respectively (USEPA OPP 2001a; USEPA OPP 2001b), these persistent compounds remain pervasive in water body sediments throughout the LMAP region 32 and 17 years, respectively, after their last legal applications. These historic-use insecticides have been studied for several decades because of their persistence and continued potential risk to aquatic biota. Comparisons of previously reported pp'-DDT and metabolites LMAP sediment contamination with this study show a slow decrease in peak Σ DDT concentrations over time with 1,275 ng g⁻¹ in 1977 (Cooper et al. 1987), 600 ng g⁻¹ in 1982 (Cooper 1991a), 129 ng g⁻¹ in 1997 (Cooper et al. 2003), and 70 ng g⁻¹ in 2000 (Moore et al. 2004). In our study, conducted in 2004, 48 of 54 sediment samples (89%) had less than 40 ng Σ DDT g⁻¹ and only five samples had more than 63 ng Σ DDT g⁻¹. Risk of ecological impairment from observed sediment contaminated with historic-use pesticides and metabolites in LMAP is considered low to moderate. Based upon sediment quality guidelines for these compounds (MacDonald et al. 2000), pp'-DDD and dieldrin rarely exceeded threshold effects concentrations (TEC; below which adverse ecological effects are unlikely) and never exceeded probable effects concentrations (PEC; above which adverse ecological effects are likely). Sediments where TECs for these compounds were exceeded occurred primarily in row-crop land-use water bodies (303d). In contrast, pp'-DDT and pp'-DDE often exceeded TECs and occasionally exceeded PECs. All row-crop land-use water body sediment samples exceeded TECs for pp'-DDT and 72% of all samples exceeded TECS for pp'-DDE. Approximately 61% and 39% of BMP-treated row-crop water body sediment samples exceeded TECs for pp'-DDT and pp'-DDE, respectively, and 83% and 17 of <1% row-crop land-use water body (NWR) sediment samples exceeded TECs for these same compounds. As a result, any impairment of

these freshwater ecosystems is likely due to the persistent organochlorine pesticide pp'-DDT and its metabolite pp'-DDE in the sediments of LMAP.

Table 4. Median (75 percentile) historic-use insecticide and metabolite concentrations (ng g⁻¹, dw) in sediments from nine watersheds in the Lower Mississippi Alluvial Plain during summer 2004 (ND= below detection limit for all six samples). Median concentrations with the same letter are not statistically significant among water bodies ($P > 0.05$).

Water Body	Fipronil	p,p'-DDT	p,p'-DDD	p,p'-DDE	Dieldrin
Upper Swan	4.1 (8.8) B	12.1 (17.9)	2.6 (3.0)	0.6 (1.2) B	0.2 (1.0) A
Lower White	1.3 (7.0) B	30.9 (111.6)	1.3 (1.6) B	0.8 (3.5) B	0.2 (0.2) A
Columbus	0 (0) A	0 (5.8) A	0 (1.0) A	0.2 (0.3) A	0 (0.2) A
Beasley	0.7 (1.1) B	6.2 (10.4) B	1.8 (3.0)	2.3 (5.2) BC	0.2 (0.2) A
Thighman	1.2 (1.5) B	4.5 (9.0) B	1.9 (3.4)	1.7 (4.2) BC	0.2 (0.3) A
Deep Hollow	0.9 (1.0) B	5.9 (10.3) B	2.3 (3.7)	2.2 (3.8) BC	0.2 (0.3) A
Bee	0.4 (5.1) B	16.4 (21.4)	2.7 (4.0)	4.6 (7.6) C	0.2 (1.9) A
Cassidy	0.1 (0.2) B	25.1 (39.5)	4.0 (4.9) C	5.2 (7.6) C	0.2 (0.2) A
Roebuck	0.2 (0.6) B	14.5 (17.4)	3.1 (3.2)	3.4 (3.8) BC	0.2 (0.2) A

To date, few studies have attempted to determine pesticide contamination within Lower Mississippi Alluvial Plain (the delta) watershed surface sediments for such a broad group of current-use chemicals (Shea et al. 2001; Moore et al. 2004). Most studies have focused primarily on persistent organochlorine insecticides such as DDT and metabolites, dieldrin, and toxaphene (Cooper et al. 1987; Cooper 1991a; Cooper 1991b; Cooper et al. 2003). Present research observed spatial patterns of surface sediment pesticide contamination among watersheds studied were due to several contributing factors. First, patterns of pesticide contamination were indicative of agricultural land-use practices in and around these watersheds with influxes of materials occurring during storm events and seasonal flooding (Shea et al. 2001; Cooper et al. 2003). Second, these patterns were further elucidated by the degree of static or flow-through conditions within each watershed, with some watersheds (Beasley Lake, BMP; Deep Hollow Lake, BMP) receiving little or no additional flow from neighboring riverine systems (Cooper et al. 2003) due to anthropogenic alteration of the landscape (e.g. drainage ditches, levees, etc.) compared with other more open watersheds (Upper Swan Lake, NWR; Lower White Lake, NWR; Columbus Lake, NWR) with extensive flood plains allowing greater transport of contaminants. Results show that despite reference (NWR) watersheds having extensive riparian areas available to process contaminants, these watersheds still receive a significant influx of current-use pesticides and that application of BMPs surrounding similar watersheds can lessen the degree of contamination.

Conclusion

Greater current-use pesticide contamination of surface sediment occurred in 2 of 3 NWR (reference) category watersheds, Upper Swan Lake and Lower White Lake. However, least contamination occurred in Columbus Lake, NWR. Use of best management practice (BMP) treatments and technologies mitigated current-use pesticide contamination of surface sediments compared to untreated watersheds (i.e. impaired, USEPA section 303d Clean Water Act). Historic-use organochlorine pesticide contamination persisted in all nine watersheds examined but was consistently lower in Columbus Lake, NWR than all other systems examined. Patterns of pesticide contamination in watershed surface sediments were influenced by agricultural land-use practices, associated storm events and seasonal flooding, and the degree of static or flow-through conditions (closed vs. open systems; Cooper et al. 2003) within each watershed.

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