

Mississippi Delta Management Systems Evaluation Area – Insecticides in Runoff, 1996-99

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INTRODUCTION

Nonpoint source contamination of our Nation's water resources has received much attention in the last decade. Potential nonpoint source contaminants include sediment, nutrients, and pesticides in watersheds that drain a variety of land use categories such as agricultural, forested, and urban areas. Although contamination due to sediment and, to a lesser degree, nutrients will most likely outweigh contamination from other nonpoint pollution sources, pesticides are probably the highest profiled and most highly publicized candidate. The concerns with pesticides not only focus on the potential impact to human health but also the impact on aquatic and wildlife habitat.

There have been many studies that have focused on the occurrence, distribution, and impact of pesticides throughout the major watersheds in the United States. Studies in the 1970's focused on the impacts of the older organochlorine insecticides on both human health and aquatic habitat integrity. Most of these compounds are no longer used in the United States. Other pesticides have been developed that have shorter life spans and are less toxic. The current-use insecticides include organophosphates (such as malathion, parathion, dimethoate) and carbamates (such as aldicarb and carbofuran). While these chemicals do not tend to bioaccumulate or persist in the environment, they can be more acutely toxic than their organochlorine predecessors. The newest group of insecticides, the synthetic pyrethroid compounds, include esfenvalerate, cyfluthrin, and cyhalothrin. Synthetic pyrethroids typically are only slightly toxic to birds and mammals but are highly toxic to fish and other aquatic animals (Rollins et al. 1997).

One of the most intensive agricultural areas of the United States is the Mississippi River Alluvial Plain in northwestern Mississippi, a 7,000-square-mile area locally referred to as the "Delta." The rich,

fertile soils of the Mississippi Delta produce a variety of crops such as cotton, soybeans, corn, and rice. The long growing season in the Mississippi Delta increases the dependency and frequency of pesticide use, especially on crops such as cotton that are highly sensitive to intense weed and insect pressures. Cotton grown in the Mississippi Delta receives about three to five times more applications of pesticides than does corn grown in the Midwest (Thurman et al. 1998). Because of the large amounts of pesticides used in the Mississippi Delta and the fact that the region is characterized with high regional rainfall (about 60 inches per year) and slightly permeable soils, there is concern for potential off-site movement of these compounds during runoff events.

The U.S. Geological Survey (USGS) began operating an automated streamflow and water-quality sampling network in the fall of 1995 as part of the Mississippi Delta Management Systems Evaluation Areas (MDMSEA) project. The primary objectives of the network are to assess the effects of conventional and alternative agricultural practices on runoff water quality to oxbow lakes (Rebich 1997).

Emphases of the USGS sampling program were placed on sediment, nutrient, and herbicide analyses. Additionally, in 1996, the USGS began providing samples to the U.S. Department of Agriculture, Agricultural Research Service (ARS), Soil and Water Research Unit, in Baton Rouge, LA, for insecticide analyses. From 1996 to 1997, the insecticide analyses included organophosphates and pyrethroids used throughout cotton-producing areas in the Mississippi Delta. However, very few samples for insecticide analyses were available in that time period due to infrequent storm events and low sample volumes. In 1998, more emphasis was placed on low-level analyses of pyrethroid insecticides, and additional samplers were installed in cooperation with industry to ensure that samples would be collected for as many runoff events as possible. The purpose of this paper is to present

selected insecticide concentration data for runoff samples collected to date for the MDMSEA project from 1996 through 1999 and to estimate the impact of watershed-level best management practices (BMP's) on the occurrence of insecticides in storm runoff.

SITE LOCATIONS AND FIELD TREATMENTS

The three MDMSEA oxbow lake watersheds are in Sunflower and Leflore Counties, Mississippi (fig.1). BMP's used in the MDMSEA project were distributed among the three watersheds by using a hierarchy approach. The streamflow and water-quality sampling network of the USGS was established to characterize the runoff in each of the three watersheds and to evaluate as many BMP's or BMP combinations as possible. The sites are distributed among the three watersheds as follows (for this paper, site names are based on USGS topographic maps, and site numbers are based on USGS downstream ordering of tributaries):

A. Thighman Lake (TL) watershed -

- Site TL2 is located on an inlet tributary of Thighman Lake. Data collected from this site will be used to compute chemical and sediment loads entering the lake during runoff events from a large area of mixed crops to the north.
- Site TL3 is an edge-of-field site located downstream of a conventional tillage cotton field, which has no BMP's. Runoff data collected at this site will be compared to data collected from sites that have BMP's.

B. Beasley Lake (BL) watershed -

- Site BL1 is an edge-of-field site that will be used to evaluate the combination of filter strips and slotted-board risers as BMP's. BL1 is located in an open-channel ditch that is grassed and drains a large area of conventional tillage cotton.
- Site BL3 is an edge-of-field site that will be used to evaluate the performance of a slotted-board riser pipe, by itself, as a BMP. Cotton has been grown at this site every year except for 1998, in which corn was grown.
- Sites BL4, BL4a, and BL4b will be used to assess the effects of a natural riparian zone on the quality of surface-water runoff. BL4 is located at the outlet

of the riparian zone upstream of the lake entrance. BL4a and BL4b are located at the entrance of the riparian zone. Most of the eastern part of the watershed, which has mixed crops of conventional cotton, soybeans, rice, and corn, drains through BL4a and BL4b and eventually through BL4.

C. Deep Hollow Lake watershed (UL stands for "unknown lake" because this particular lake is not named on the USGS topographic map) -

- Site UL1 drains both soybean and cotton fields that will have the combination of conservation tillage and winter cover crops for BMP's. In addition, the culvert entrance at UL1 has a slotted-board riser.
- Site UL2 also drains fields planted in both soybean and cotton and will have a combination of conservation tillage and winter cover crops as BMP's.

MATERIALS AND METHODS

The pyrethroid insecticides lambda-cyhalothrin, cypermethrin, cyfluthrin, and deltamethrin and the organophosphate insecticides methyl parathion and azinphosmethyl were selected for this study due to their popularity and use among MDMSEA farmers. The following sections provide some background information about these particular insecticides, the sampling methods, and the method of analyses used in this study.

Background Information

Pyrethroids. The synthetic pyrethroid insecticides are derivatives of natural pyrethroids known for centuries to have insecticidal activity. The most important natural pyrethroid, pyrethrum, is isolated from the heads of chrysanthemums (Capel and Nelson 1995). Synthetic pyrethroids, first developed in 1973, are more stable to light and possess a higher insecticidal activity, almost ten times that of most organophosphorus and carbamate insecticides (Elliot et al. 1987). The stability and activity of the synthetic pyrethroids are reflected in their increased use during the last two decades on fruits, vegetables, corn, and especially cotton. The high insecticidal activities of these chemicals allow relatively small amounts to be applied (about 100 grams per hectare). Selected chemical and physical properties of the pyrethroids examined in this study

are listed in table 1.

Pyrethroid insecticides in general can be used to control a wide range of pests in a variety of applications in both agricultural and urban/household settings. The acute toxicity of these chemicals is typically moderate when considering the oral route of exposure in laboratory animals but can be fairly high when considering inhalation and dermal routes of exposure. These chemicals typically cause very few if any reproductive, carcinogenic, or mutagenic effects. These chemicals are only slightly toxic to birds and other mammals but are highly toxic to fish and other aquatic invertebrate species. For example, the LC50 for lambda-cyhalothrin is 0.24 ug/L (micrograms per liter) in rainbow trout. The potential for these chemicals to bioconcentrate or bioaccumulate in aquatic species exists but is typically rare and causes minimal toxic effects (EXTOXNET-PIP 1996).

With regard to mobility, these chemicals are practically insoluble in water and bind to organic materials and sediment fairly rapidly. Therefore, their mobility in surface waters would emulate the mobility of organic materials and sediment during runoff events. As BMP's are implemented to reduce erosion and sedimentation from agricultural fields, it is likely that the same BMP's will decrease pyrethroid contributions to receiving waters such as oxbow lakes.

Organophosphates. Organophosphates were developed in the early 1800's, but their effects on insects, which are similar to their effects on humans, were not discovered until 1932. Organophosphates affect an insect's nervous system by reducing the ability of the enzyme, cholinesterase, to function properly in regulating nerve impulses from a nerve cell to a muscle cell or another nerve cell resulting in symptoms such as weakness or paralysis. Organophosphates account for about half of all insecticides sold in the United States. In addition to use on major crops such as cotton, corn, and wheat, they a organophosphates are used on many important minor crops. Some also are used for mosquito control to protect public health against diseases such as malaria, dengue fever, and encephalitis. The wide use of organophosphates is based on several factors: (1) relatively inexpensive; (2) broad spectrum - most organophosphates can be used on several crops to control a variety of

insect pests; (3) because of this broad spectrum of activity, one organophosphate might control the insects that would require three or four non-organophosphate insecticides; and (4) in general, insects have not developed resistance to organophosphates as they have to some other pesticides (USEPA 1999).

Organophosphates typically are highly toxic when exposed to laboratory animals in acute toxicity tests, regardless of the method of exposure (inhalation, dermal, ingestion, or eye contact). However, these chemicals typically do not cause reproductive, mutagenic, or carcinogenic effects. Methyl parathion is highly toxic to birds and other mammals, but azinphosmethyl is only slightly to moderately toxic to birds and other mammals. Azinphosmethyl is highly toxic to both fish and other aquatic organisms, whereas methyl parathion is moderately toxic to fish but highly toxic to other aquatic organisms (EXTOXNET-PIP 1996). Selected chemical and physical properties of the organophosphates examined for this study are listed in table 1.

Both methyl parathion and azinphosmethyl degrade quickly and have a moderate tendency to attach to organic materials. It is likely, then, that the only potential risks from these chemicals on receiving waters would occur during runoff events shortly after applications. BMP's that are implemented to reduce erosion and sedimentation within agricultural watersheds should somewhat reduce contributions of organophosphate insecticides to receiving waters.

Sample Collection

The samples collected during this study were all flow-weighted composite samples from automated samplers installed at each site. The samplers are stage-activated and deposit aliquots of water into sample containers each time a pre-determined runoff volume passes the sampling point. Thus, each sample represents an average concentration of insecticides in the runoff water per storm. These samples are not filtered prior to shipment. Quality assurance /quality control (QA/QC) measures were adopted to avoid possible contamination to the samples. Specific items of the QA/QC program that were adopted for the MDMSEA project are as follows:

- The sample bottles are glass and are cleaned in the lab prior to field use as

follows: de-ionized (DI) water rinse, non-phosphorus detergent rinse, DI water rinse.

- All sampler tubing used for sampler intake lines is made of Teflon.
- Samples are shipped to laboratories for analyses within 48 hours after a sampling event.
- Field blanks will be taken at least four times per year (or more if time allows): winter, early spring, late spring, and summer.
- If analyses of the field blanks indicate concentrations above the detection limits, then appropriate action will be taken to identify and eliminate the source of contamination.
- Laboratories will provide additional QA/QC as samples are received, processed, and analyzed.

Sample Analyses

Samples collected from 1996 through 1997 were analyzed by the ARS Soil and Water Research Unit, in Baton Rouge, LA. The method for analyses by ARS for both pyrethroids and organophosphates was extraction (water and sediment combined) with ethyl acetate and analysis by gas chromatography (electron capture detection). The detection limits using this method for the pyrethroids were 400 and 600 parts per trillion (ppt) for cypermethrin and cyfluthrin, respectively. The detection limits for the organophosphates were 200 and 500 parts per trillion for methyl parathion and azinphosmethyl, respectively.

As stated earlier, additional samplers were installed in 1998 to ensure that enough sample was collected for insecticide analyses, specifically pyrethroids. The ARS lab continued to be used for organophosphate analyses; however, a contract lab was used for pyrethroid analyses. The contract lab was used so that different methods could be developed with lower limits of detection. For 1998, the detection limits were 50 ppt for lambda-cyhalothrin and 125 ppt for cypermethrin, cyfluthrin, and deltamethrin. Additional work was done with method development in 1999 (all samples after January 8) to lower the detection limits for each pyrethroid to 10 ppt. In general, the current pyrethroid method used by the contract lab requires the sample to be extracted (water and sediment

combined) in the original sample container with hexane and then analyzed by gas chromatography/mass selective detector (GC/MSD) technology.

RESULTS AND DISCUSSION

Pyrethroids

Dates of application of pyrethroids to fields upstream of the sampling sites are listed in table 2. Selected pyrethroid concentrations in runoff samples are listed in table 3. Concentrations of pyrethroids for samples collected more than one year after application are not included in table 3. Because the USGS sampling program prioritized the analyses of sediment, nutrients, and herbicides, there was only enough water available for seven runoff samples from three sites from 1996 to 1997 for pyrethroid analyses. In 1996, there were only six runoff samples collected between 30 and 188 days after application. Pyrethroid concentrations were all below the detection limits. In 1997, only one runoff sample (from UL1) was collected, and it had pyrethroid concentrations below detection limits. Therefore, there were not enough data to adequately assess the effects of BMP's on pyrethroid insecticides in the MDMSEA watersheds for the 1996-97 period.

In 1998, after additional samplers were installed, 23 samples were collected from April 27 to December 11 (in table 3 for 1998, refer to 1997 applications for days after application greater than 200). No runoff sample collected during 1998 contained pyrethroids above the detection limits. Runoff that occurs within 1 month of application has the best opportunity to contain measurable pyrethroid content. During the 1998 season, there were only two runoff events that occurred less than 1 month after application. Both of these events were at the UL1 site, which has conservation tillage cotton and soybeans and a slotted-board riser as BMP's. The runoff event that occurred on May 28 was 8 days after application of lambda-cyhalothrin and 20 days after cypermethrin application. The June 15 runoff event occurred 26 days after application of lambda-cyhalothrin and only 3 days after the second application of cypermethrin. The failure to detect the applied compounds within the first month, especially within the first 2 weeks of application, can be explained by possible low sediment loads, low application rates (80 milliliters per hectare, 0.03 kilograms per hectare

active ingredient), higher than expected degradation rates, insufficiently sensitive limits of detection, or false negative analyses (not detecting pyrethroids when present).

In 1999, 37 samples were collected from January 8 to December 12 (in table 3 for 1999, refer to 1998 applications for days after application greater than 150). There were a total of four detects of pyrethroids within the 1999 sampling period. On May 4, 5 days after application, the concentration of cypermethrin was 100 ppt at BL4a, which is the entrance of the large riparian area at Beasley Lake.

For that same runoff event, no cypermethrin was detected at the exit site BL4. A lambda-cyhalothrin concentration of 30 ppt was measured at the entrance (BL4a), and a concentration of 20 ppt was measured at the exit (BL4) for the May 4-5 event. According to farm records, however, lambda-cyhalothrin had not been applied at these sites since the previous growing season. Possible explanations for these two lambda-cyhalothrin detections include:

(1) a non-recorded application within 1 month of the runoff event, (2) a misapplication of the chemical, or (3) false positive analyses, which is the detection of pyrethroids when none are present. On May 31, 10 days after a known application, lambda-cyhalothrin was detected at BL4a at a concentration of 20 ppt.

In all cases of detection, the concentrations were lower than toxic levels for aquatic species and were likely not bio-available in the water column because of sorption to suspended sediment.

Pyrethroids exhibit low water solubilities and are typically expected to travel in runoff sorbed to suspended sediment. The detections that occurred in 1999 were primarily at the BL4a site in the Beasley watershed, which is located at the entrance of the riparian zone and drains a large area of conventional tillage row crops. Such conditions could suggest that the quality of the water entering the riparian area is characterized by excessive sediment in the runoff. However, the median suspended-sediment concentration for BL4a for the period of record is 399 mg/L (milligrams per liter), which is low for runoff from a conventional tillage field. Therefore, it is unlikely that the detections of pyrethroids at BL4a in 1999 were due to excessive sediment.

There were numerous other samples collected during runoff events in 1999 that occurred within 1 month of application but did not have detectable

concentrations of pyrethroids. One of these events occurred within 4 days after application of cyfluthrin. These non-detects occurred at locations such as the riparian exit in the Beasley watershed and at both sites in the Deep Hollow watershed, which contains conservation tillage. For these locations, the quality of the runoff water is characterized by fairly low sediment concentrations compared to sediment concentrations in runoff from conventional tillage. The median suspended-sediment concentration for the period of record at BL4 and UL1 is 201 and 748 mg/L, respectively, which is low compared to the median suspended-sediment concentration at TL3 of 1,317 mg/L. Because no pyrethroids were applied at the TL3 site in 1999, the ability of the BMP's to reduce pyrethroids with respect to sediment loads cannot be evaluated.

Some quality control samples were collected to evaluate bias and variability in the data. Field blanks are used to determine biases caused by contamination during sample collection and handling. No field blanks collected to date had detectable levels of pyrethroids. Field matrix spike samples can be used to evaluate the variability due to degradation during sample collection, processing, shipping, and holding and to evaluate the variability in the lab analyses. Unfortunately, no field matrix spikes were sent to the laboratories with the pyrethroid samples at any time during this study. Lab matrix spikes are also used to evaluate the variability in the lab analyses. Lab matrix spikes were analyzed for each set of samples received. Percent recoveries were included with the environmental results. With regard to the detections of pyrethroids on May 4 and 31, 1999, at BL4a and May 5, 1999, at BL4, the percent recoveries were all within acceptable limits indicating that false positive analyses caused by lab variability was not likely. With regard to the potential of false negative results, there were only a few samples in which the percent recoveries were marginal. For the July 21, 1999, sample at UL1, the percent recovery for lambda-cyhalothrin was 77 percent. For the August 7, 1999, samples at UL1 and UL2, the percent recoveries for cyfluthrin and deltamethrin were 60 and 72 percent, respectively. The marginal percent recoveries for these three samples could indicate false negative analyses, but without field matrix spikes, this cannot be verified.

Organophosphates

Application of methyl parathion and azinphosmethyl in the MDMSEA watersheds for 1996 through 1998 is summarized in table 4. Concentrations of these two organophosphate insecticides in runoff samples collected during the same time period are listed in table 5. Concentrations of organophosphates for samples collected more than 1 year after application are not included in table 5. These two organophosphates were not applied in 1999. Eight runoff events were sampled after application of methyl parathion in 1996 (11 to 108 days after application). Five runoff events were sampled after application of methyl parathion in 1997 (1 to 24 days after application). Eleven runoff events were sampled after application of methyl parathion in 1998 (72 to 122 days after application). It is likely that more runoff events occurred during each of these years; however, enough sample was available only for these few sampling events. In all cases, methyl parathion was not detected, even in the samples collected from BL4 and BL1 in 1997 in which a runoff event occurred 1 and 3 days after application, respectively. The likely reason for no detection is that methyl parathion has a short soil half-life thus degrading rapidly before being mobilized during a runoff event. The non-detects occurring shortly after application could also be the result of the locations of the sites in the watershed and their associated BMP's. BL4 is the exit site of the riparian zone as stated before, and BL1 has a long, grassed waterway prior to the sampling point. Both of these field conditions could accelerate degradation and processing of methyl parathion prior to sampling. However, not enough data exist to evaluate the benefits of the BMP's in reducing methyl parathion concentrations in the runoff.

Three runoff events occurred after application of azinphosmethyl in 1998 (109 to 136 days after application). There were no detections of azinphosmethyl in these samples. The soil half-life of azinphosmethyl is reported to be 10 days (table 1). Therefore, it is likely that azinphosmethyl degraded prior to these runoff events.

SUMMARY

The USGS began operating an automated streamflow and water-quality sampling network in the fall of 1995 as part of the MDMSEA project. In 1996, the USGS began providing samples to ARS

for insecticide analyses. From 1996 to 1997, the insecticide analyses included organophosphates and pyrethroids used throughout cotton-producing areas in the Mississippi Delta. However, very few samples for insecticide analyses were available in that time period due to infrequent storm events and low sample volumes. In 1998, more emphasis was placed on low-level analyses of pyrethroid insecticides, and additional samplers were installed to ensure that samples would be collected for as many runoff events as possible.

For pyrethroid samples collected from 1996 to 1999, there were a total of four detects of pyrethroids, which occurred in the 1999 sampling period. These detections occurred shortly after application; however, there were other samples collected shortly after application that had no detections. The fact that detections occurred at some sites and not others shortly after application could suggest that sediment concentrations were elevated at some locations but not others. However, no adequate conclusions could be drawn to evaluate the ability of the BMP's to reduce pyrethroids with respect to sediment loads. The failure to detect the applied compounds within the first month after application can also be explained by low application rates (80 milliliters per hectare), higher than expected degradation rates, insufficiently sensitive detection limits early in the study, or the possibility of false negative analyses. However, not enough data exists to verify any of these conclusions.

Neither methyl parathion nor azinphosmethyl were detected in any of the samples from 1996 through 1998. The likely reason for no detection is that both compounds have short soil half-lives, thus degrading rapidly before mobilizing during a runoff event. Not enough data exists to evaluate the benefits of BMP's in reducing methyl parathion or azinphosmethyl concentrations in the runoff.

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Table 1. Chemical properties of selected insecticides. ^a

[Sw, solubility in water; Koc, soil organic carbon partition coefficient; $t_{1/2}$, half-life; mg/L, milligrams per liter; mL/g, milliliters per gram]

| Insecticide | Sw (mg/L) | Koc (mL/g) | Soil $t_{1/2}$ (days) | Leaf $t_{1/2}$ (days) |
|--------------------|--------------|---------------|--------------------------|--------------------------|
| Lambda-cyhalothrin | 0.005 | 180,000 | 30 | 10 |
| Cypermethrin | 0.01 | 100,000 | 30 | 10 |
| Cyfluthrin | 0.002 | 100,000 | 30 | 10 |
| Deltamethrin | 0.002 | 100,000 | 30 | 10 |
| Methyl Parathion | 60 | 5,100 | 5 | 0.1 |
| Azinphosmethyl | 29 | 1,000 | 10 | 1 |

^a Data from Hornsby et al. 1996; Willis et al. 1992; and EXTOWNET-PIP 1996. All leaf $t_{1/2}$ values estimated except for methyl parathion.

Table 2. Pyrethroid applications at MDMSEA sites, 1996-99

[-----, no pyrethroid insecticides applied; *****, runoff samplers not installed]

| Site | Lambda-cyhalothrin | Cypermethrin | Cyfluthrin | Deltamethrin |
|-------------|--------------------------------|---------------------|----------------------------|--------------|
| 1996 | | | | |
| TL2 | ----- | ----- | Jun 19; Jul 26; Aug 14, 24 | ----- |
| TL3 | ----- | ----- | ----- | ----- |
| BL1 | Jun 12; Jul 11, 17, 25; Aug 17 | ----- | ----- | ----- |
| BL3 | ----- | ----- | ----- | ----- |
| BL4a | ***** | ***** | ***** | ***** |
| BL4b | ***** | ***** | ***** | ***** |
| BL4 | ***** | ***** | ***** | ***** |
| UL1 | May 24; Jul 15 | May 3 | Jun 1 | ----- |
| UL2 | May 24; Jul 15 | May 3 | Jun 1 | ----- |
| 1997 | | | | |
| TL2 | ----- | ----- | ----- | ----- |
| TL3 | ----- | ----- | ----- | ----- |
| BL1 | Aug 21; Sep 1 | ----- | Jun 17, 21, 24; Jul 2 | ----- |
| BL3 | ----- | ----- | Jun 21, 24 | ----- |
| BL4a | Jul 19 | ----- | Jun 20 | ----- |
| BL4b | ----- | ----- | ----- | ----- |
| BL4 | Jul 19 | ----- | Jun 20 | ----- |
| UL1 | Aug 3, 16 | Jul 20 | Jul 10 | ----- |
| UL2 | Aug 3, 16 | Jul 20 | Jul 10 | ----- |
| 1998 | | | | |
| TL2 | May 1; Jun 5; Aug 8 | ----- | ----- | ----- |
| TL3 | Jun 14 | ----- | ----- | ----- |
| BL1 | ----- | ----- | ----- | ----- |
| BL3 | ----- | ----- | ----- | ----- |
| BL4a | Jun 17, 26 | ----- | Jun 1; Jul 10, 15, 22, 27 | ----- |
| BL4b | ----- | ----- | ----- | ----- |
| BL4 | Jun 17, 26 | ----- | Jun 1; Jul 10, 15, 22, 27 | ----- |
| UL1 | May 20; Jul 1, 7 | May 8; Jun 3; Aug 1 | ----- | Aug 11 |
| UL2 | May 20; Jul 1, 7 | May 8; Jun 8; Aug 1 | ----- | Aug 11 |
| 1999 | | | | |
| TL2 | Jul 18 | Aug 5 | ----- | ----- |
| TL3 | ----- | ----- | ----- | ----- |
| BL1 | Jul 8; Aug 13 | May 9 | ----- | ----- |
| BL3 | Jul 8; Aug 13 | ----- | ----- | ----- |
| BL4a | May 18 | Apr 29 | ----- | ----- |
| BL4b | May 13, 21; Jul 12 | ----- | ----- | ----- |
| BL4 | May 13, 18, 21; Jul 12 | Apr 29 | ----- | ----- |
| UL1 | May 30; Jun 15; Jul 31; Aug 14 | May 11; Aug 14 | Jun 9; Jul 17; Aug 14 | Jul 24 |
| UL2 | Jun 15; Jul 31; Aug 14 | May 9; Aug 14 | Jun 9; Jul 17; Aug 14 | Jul 24 |

Table 3. Concentration of pyrethroids in runoff from MDMSEA watersheds, 1996-1999

[ppt, parts per trillion; DAA, days after application; ^a, ARS data; ^b, contract lab data]

| Site | Runoff event date | Lambda-cyhalothrin ppt (DAA) | Cypermethrin ppt (DAA) | Cyfluthrin ppt (DAA) | Deltamethrin ppt (DAA) |
|--------------------------|-------------------|------------------------------|------------------------|----------------------|------------------------|
| 1996 ^a | | | | | |
| TL3 | Oct 26 | | | < 600 (63) | |
| TL3 | Nov 7 | | | < 600 (75) | |
| UL1 | Aug 2 | | < 400 (91) | < 600 (30) | |
| UL2 | Oct 25 | | < 400 (175) | < 600 (114) | |
| UL2 | Nov 1 | | < 400 (182) | < 600 (121) | |
| UL2 | Nov 7 | | < 400 (188) | < 600 (127) | |
| 1997 ^a | | | | | |
| UL1 | Jul 13 | | | < 600 (3) | |
| 1998 ^b | | | | | |
| TL2 | Nov 14 | < 50 (98) | | | |
| TL2 | Dec 11 | < 50 (125) | | | |
| BL1 | Apr 28 | < 50 (240) | | < 125 (300) | |
| BL3 | May 29 | | | < 125 (339) | |
| BL4a | May 28 | < 50 (313) | | < 125 (342) | |
| BL4a | Nov 14 | < 50 (141) | | < 125 (110) | |
| BL4a | Nov 20 | < 50 (147) | | < 125 (116) | |
| BL4a | Dec 10 | < 50 (167) | | < 125 (136) | |
| BL4a | Dec 11 | < 50 (168) | | < 125 (137) | |
| BL4 | May 29 | < 50 (314) | | < 125 (343) | |
| UL1 | Apr 27 | < 50 (254) | < 125 (281) | < 125 (291) | |
| UL1 | May 28 | < 50 (8) | < 125 (20) | < 125 (322) | |
| UL1 | Jun 15 | < 50 (26) | < 125 (12) | < 125 (340) | |
| UL1 | Nov 14 | < 50 (130) | < 125 (105) | | < 125 (95) |
| UL1 | Nov 20 | < 50 (136) | < 125 (111) | | < 125 (101) |
| UL1 | Dec 7 | < 50 (153) | < 125 (128) | | < 125 (118) |
| UL1 | Dec 10 | < 50 (156) | < 125 (131) | | < 125 (121) |
| UL1 | Dec 11 | < 50 (157) | < 125 (132) | | < 125 (122) |
| UL2 | Apr 28 | < 50 (255) | < 125 (282) | < 125 (292) | |
| UL2 | Apr 30 | < 50 (257) | < 125 (284) | < 125 (294) | |
| UL2 | Nov 14 | < 50 (130) | < 125 (105) | | < 125 (95) |
| UL2 | Dec 7 | < 50 (153) | < 125 (128) | | < 125 (118) |
| UL2 | Dec 11 | < 50 (157) | < 125 (132) | | < 125 (122) |

Table 3. Concentration of pyrethroids in runoff from MDMSEA watersheds, 1996-1999 ... *continued*[ppt, parts per trillion; DAA, days after application; ^a, ARS data; ^b, contract lab data]

| Site | Runoff event date | Lambda-cyhalothrin ppt (DAA) | Cypermethrin ppt (DAA) | Cyfluthrin ppt (DAA) | Deltamethrin ppt (DAA) |
|-------------------------|-------------------|------------------------------|------------------------|----------------------|------------------------|
| 1999^b | | | | | |
| TL2 | Jan 8 | < 50 (153) | | | |
| TL3 | Jan 8 | < 50 (208) | | | |
| TL3 | Apr 3 | < 10 (293) | | | |
| TL3 | Apr 14 | < 10 (304) | | | |
| BL1 | May 31 | | < 10 (22) | | |
| BL1 | Jun 2 | | < 10 (24) | | |
| BL4a | Jan 8 | < 50 (196) | | < 125 (165) | |
| BL4a | Mar 2 | < 10 (249) | | < 10 (218) | |
| BL4a | Mar 13 | < 10 (260) | | < 10 (229) | |
| BL4a | Apr 3 | < 10 (281) | | < 10 (250) | |
| BL4a | Apr 5 | < 10 (283) | | < 10 (252) | |
| BL4a | Apr 14 | < 10 (292) | | < 10 (261) | |
| BL4a | May 4 | 30 (312) | 100 (5) | < 10 (281) | |
| BL4a | May 31 | 20 (13) | < 10 (32) | | |
| BL4a | Nov 2 | < 10 (167) | < 10 (186) | | |
| BL4a | Dec 12 | < 10 (208) | < 10 (227) | | |
| BL4b | Dec 12 | < 10 (153) | | | |
| BL4 | Jan 8 | < 50 (196) | | < 125 (165) | |
| BL4 | Mar 13 | < 10 (260) | | < 10 (229) | |
| BL4 | Apr 4 | < 10 (282) | | < 10 (251) | |
| BL4 | Apr 6 | < 10 (284) | | < 10 (253) | |
| BL4 | Apr 14 | < 10 (292) | | < 10 (261) | |
| BL4 | May 5 | 20 (313) | < 10 (6) | < 10 (282) | |
| UL1 | Jan 8 | < 50 (185) | < 125 (160) | | < 125 (150) |
| UL1 | Mar 2 | < 10 (238) | < 10 (213) | | < 10 (203) |
| UL1 | Mar 13 | < 10 (249) | < 10 (224) | | < 10 (214) |
| UL1 | Apr 3 | < 10 (270) | < 10 (245) | | < 10 (235) |
| UL1 | Apr 14 | < 10 (281) | < 10 (256) | | < 10 (246) |
| UL1 | Jul 14 | < 10 (29) | < 10 (65) | < 10 (26) | |
| UL1 | Jul 21 | < 10 (36) | < 10 (71) | < 10 (4) | |
| UL1 | Aug 7 | < 10 (7) | < 10 (88) | < 10 (21) | < 10 (14) |
| UL2 | Jan 8 | < 50 (185) | < 125 (160) | | < 125 (150) |
| UL2 | Mar 12 | < 10 (248) | < 10 (223) | | < 10 (213) |
| UL2 | Apr 3 | < 10 (270) | < 10 (245) | | < 10 (235) |
| UL2 | Apr 14 | < 10 (281) | < 10 (256) | | < 10 (246) |
| UL2 | Jul 15 | < 10 (30) | < 10 (66) | < 10 (27) | |
| UL2 | Aug 7 | < 10 (7) | < 10 (90) | < 10 (21) | < 10 (14) |

Table 4. Organophosphate applications at MDMSEA sites, 1996-98

[-----, no organophosphate insecticides applied; *****, runoff samplers not installed]

| Site | Methyl Parathion | Azinphosmethyl |
|-------------|---|----------------|
| <u>1996</u> | | |
| TL2 | Jun 6, 26; Jul 15, 17, 19; Aug 1, 8, 14, 24; Sept 1 | ----- |
| TL3 | Jun 6, 26; Jul 15, 17, 19; Aug 1, 8, 14, 24; Sept 2 | ----- |
| BL1 | Jun 5, 12; Jul 7, 11, 20; Aug 31 | ----- |
| BL3 | Jun 5; Jul 7, 11, 26; Aug 3, 17 | ----- |
| BL4a | ***** | ***** |
| BL4b | ***** | ***** |
| BL4 | ***** | ***** |
| UL1 | Jun 8; Jul 10, 15, 22 | ----- |
| UL2 | Jun 8; Jul 10, 15, 22 | ----- |
| <u>1997</u> | | |
| TL2 | ----- | ----- |
| TL3 | ----- | ----- |
| BL1 | Jun 4, 10; Jul 2, 15, 21; Aug 6; Sept 3, 12 | ----- |
| BL3 | May 25; Jun 4, 10, 28; Jul 21; Aug 23; Sept 6 | ----- |
| BL4a | Jun 14, 16, 28; Jul 7, 10, 16, 22 | ----- |
| BL4b | ----- | ----- |
| BL4 | Jun 14, 16, 28; Jul 7, 10, 16, 22 | ----- |
| UL1 | Jun 3, 11, 24 | ----- |
| UL2 | Jun 3, 11, 24 | ----- |
| <u>1998</u> | | |
| TL2 | ----- | ----- |
| TL3 | ----- | ----- |
| BL1 | ----- | ----- |
| BL3 | ----- | ----- |
| BL4a | Jun 1, 3, 9, 17, 26; Jul 30; Aug 3, 4, 10, 11 | Jul 28 |
| BL4b | ----- | ----- |
| BL4 | Jun 1, 3, 9, 17, 26; Jul 30; Aug 3, 4, 10, 11 | Jul 28 |
| UL1 | Sept 3 | ----- |
| UL2 | Sept 3 | ----- |

Table 5. Concentration of organophosphate insecticides in runoff from MDMSEA watersheds, 1996-98

[ppt, parts per trillion; DAA, days after application]

| Site | Runoff event date | Methyl Parathion ppt (DAA) | Azinphosmethyl ppt (DAA) |
|-------------|-------------------|----------------------------|--------------------------|
| <u>1996</u> | | | |
| TL3 | Oct 26 | < 200 (55) | |
| TL3 | Nov 7 | < 200 (67) | |
| BL3 | Nov 1 | < 200 (76) | |
| BL3 | Nov 7 | < 200 (82) | |
| UL1 | Aug 2 | < 200 (11) | |
| UL2 | Oct 25 | < 200 (95) | |
| UL2 | Nov 1 | < 200 (102) | |
| UL2 | Nov 7 | < 200 (108) | |
| <u>1997</u> | | | |
| BL1 | Aug 9 | < 200 (3) | |
| BL4 | Jul 8 | < 200 (1) | |
| BL4 | Aug 9 | < 200 (18) | |
| BL4 | Aug 14 | < 200 (23) | |
| BL4 | Aug 15 | < 200 (24) | |
| <u>1998</u> | | | |
| BL4a | Nov 14 | < 200 (95) | < 500 (109) |
| BL4a | Dec 10 | < 200 (121) | < 500 (135) |
| BL4a | Dec 11 | < 200 (122) | < 500 (136) |
| UL1 | Nov 14 | < 200 (72) | |
| UL1 | Nov 20 | < 200 (78) | |
| UL1 | Dec 7 | < 200 (95) | |
| UL1 | Dec 10 | < 200 (98) | |
| UL1 | Dec 11 | < 200 (99) | |
| UL2 | Nov 14 | < 200 (72) | |
| UL2 | Dec 7 | < 200 (95) | |
| UL2 | Dec 11 | < 200 (99) | |

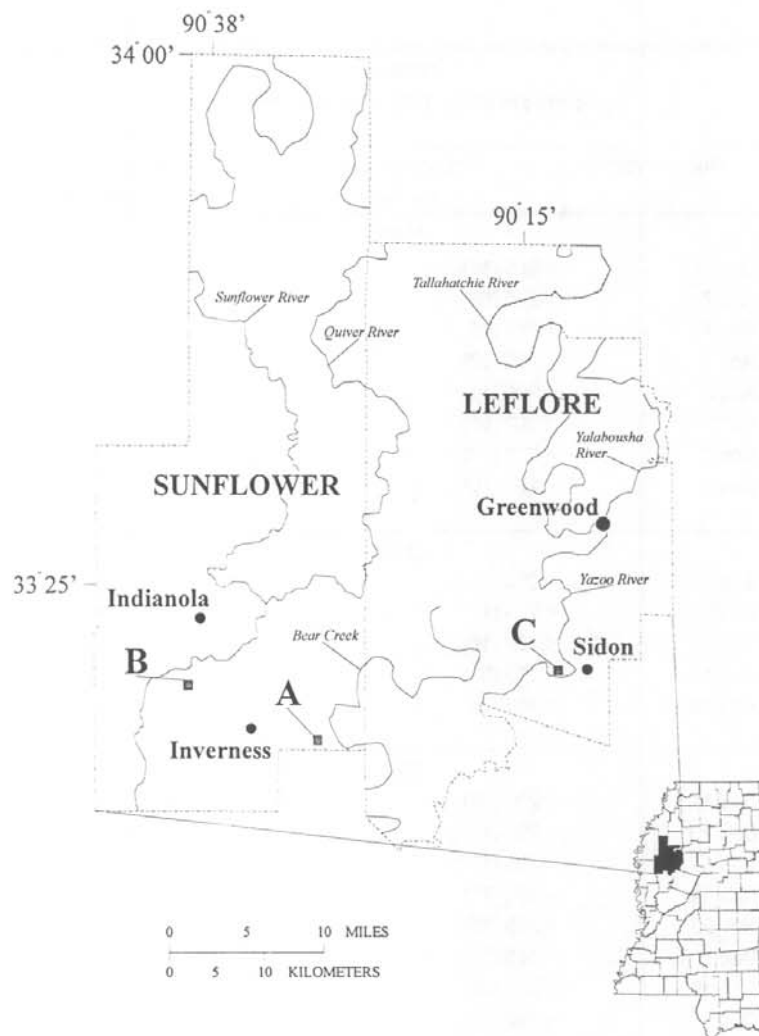


Figure 1. Mississippi Delta MSEA study watersheds and runoff monitoring site locations: A) Thighman Lake watershed; B) Beasley Lake watershed; C) Deep Hollow Lake watershed.