



Occurrence of Cotton Pesticides in Surface Water of The Mississippi Embayment

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This fact sheet introduces a study of the nonpoint-source occurrence of pesticides in water of the cotton-growing areas of the Southern United States with special emphasis on the Mississippi Embayment (fig. 1). This study is being conducted by the U.S. Geological Survey (USGS) Organic Geochemistry Research Group, which investigates the fate and transport of agricultural chemicals in the environment. The purpose of this fact sheet is to give an overview of the cotton-growing areas of the United States, to provide usage data for cotton pesticides in the United States, to present information on the types of pesticide compounds and concentrations that have been found thus far in the Mississippi Embayment, and to discuss current areas of cotton pesticide research.

Introduction

Contamination of water in the Midcontinental United States from pesticide application to row crops (corn and soybeans) has been a major water-quality issue during the past decade. Perhaps equally important to water quality in the Southern United States is the application of pesticides to cotton, which receives three to five times greater application of pesticides per acre than does corn or soybeans. In spite of the greater use of pesticides, few regional water-quality studies have addressed pesticide occurrence in water of the Southern United States.

Cotton-growing areas of the United States (fig. 1) extend from the East Coast (The Carolinas) to the Mississippi Embayment, the Texas High Plains, and the arid deserts of the Southwest (Arizona and California). These areas of the country have different climate, precipitation, and soil types, which result in different weed and insect pressures, as well as different runoff potentials; therefore, pesticide-usage, runoff, and leaching patterns are often different. Because of these considerations, the types and amounts of pesticides applied may vary considerably throughout the

cotton-growing areas. For example, fluometuron is a cotton herbicide used primarily in Mississippi and in the eastern coastal plain (fig. 2; Battaglin and Goolsby, 1995) but is little used in other cotton-growing areas.

The geographic usage information displayed in figure 2 can be useful for designing regional water-quality surveys and for methods-development strategies for a compound such as fluometuron. Another method to visualize cotton pesticide usage in the United States is the bar graph shown in figure 3. The compounds shown account for nearly all of the pesticides used in cotton-growing

areas (Gianessi and Anderson, 1995). The three most-used pesticides are herbicides (monosodium methylarsonate, trifluralin, and fluometuron).

Study Area

A major area for cotton production in the United States is the Mississippi Embayment (fig. 4). The area consists of parts of Arkansas, Kentucky, Louisiana, Mississippi, Missouri, and Tennessee. Rainfall amounts of as much as 60 inches per year and relatively flat, only slightly permeable soils characterized by large runoff volumes and low relief are typical of this area. Major pesticides used in the

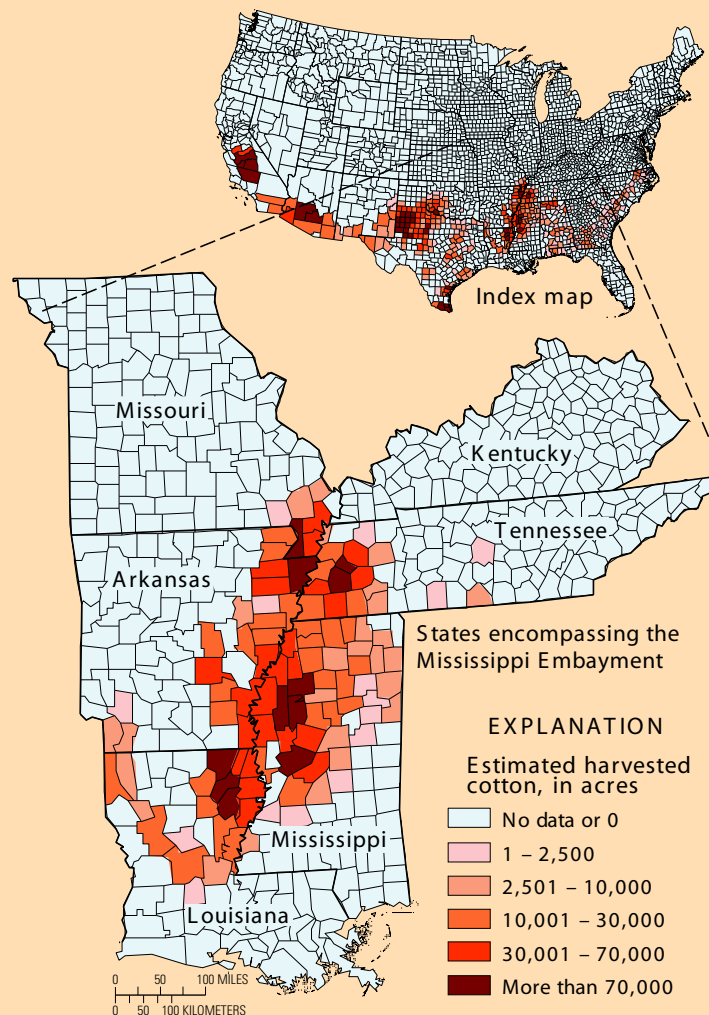


Figure 1. Estimated harvested cotton in the United States, 1987 (data from Battaglin and Goolsby, 1995)

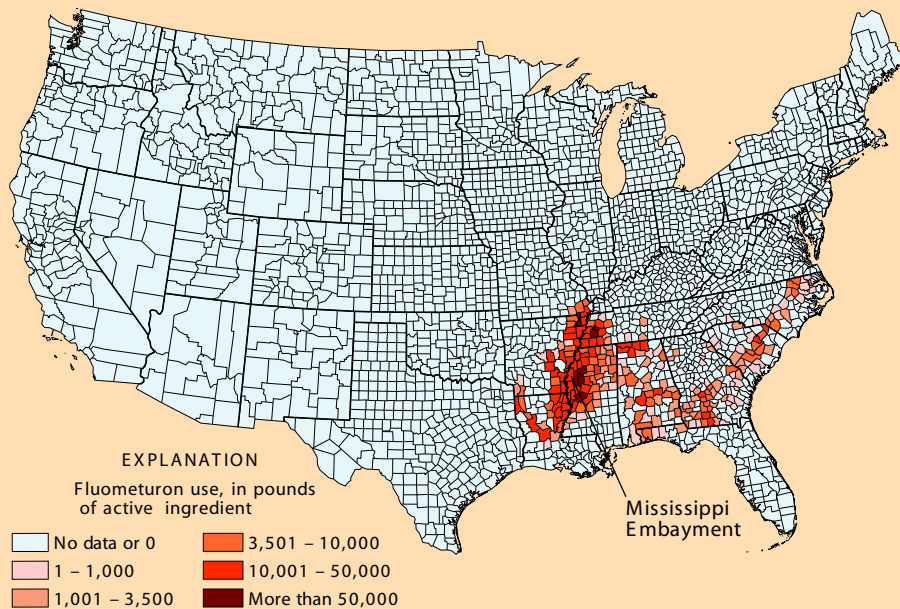


Figure 2. Fluometuron use in cotton-growing areas of the United States, 1987 (data from Battaglin and Goolsby, 1995).

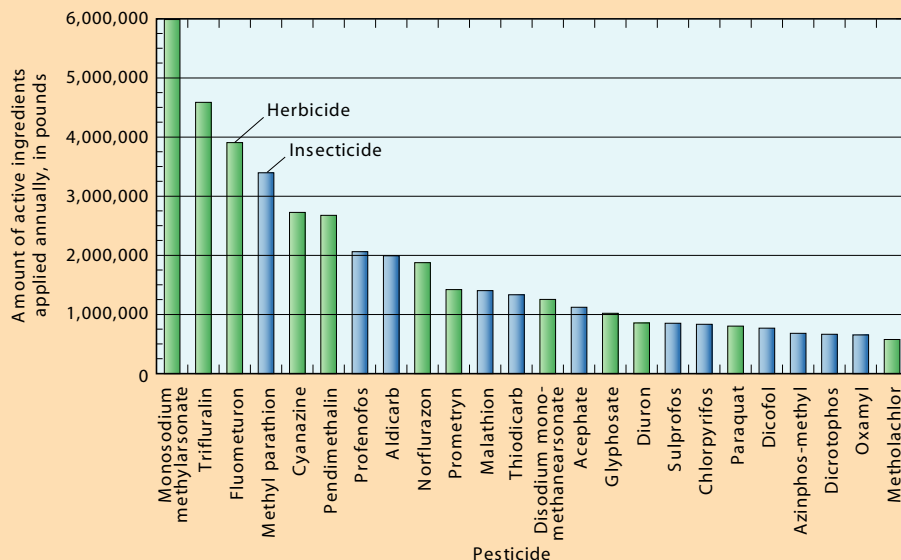


Figure 3. Cotton pesticide usage in the United States, 1990-93 (data from Gianessi and Anderson, 1995).

area include monosodium methylarsenate, fluometuron, cyanazine, pendimethalin, methyl parathion, and trifluralin.

Methods of Study

Surface-water samples were collected at 64 sites in the Mississippi Embayment from January-December 1996 in conjunction with the USGS National Water-Quality Assessment (NAWQA) Program. The location of the sampling sites is shown in figure 4. Fixed sites were sampled weekly for 1 year, and reconnaissance sites were sampled one time. Samples were filtered through glass-fiber filters (1.0 micron) and stored on ice until analyzed at the USGS laboratory in Lawrence, Kansas.

Water samples were extracted and analyzed by gas chromatography/mass spectrometry (GC/MS) for the detection and quantitation of the major cotton pesticides. The method consists of using solid-phase extraction (SPE) for the isolation of the compounds followed by elution with ethyl acetate (an organic solvent) and analysis by gas chromatography with identification by mass spectrometry using selected ion detection (Thurman and others, 1990). The detection limit was 0.05 µg/L (micrograms per liter) for all herbicides and 0.01 µg/L for all insecticides.

In addition to the standard approach of GC/MS for chemical analyses, other methods for the evaluation of pesticides

in the aquatic environment are being used. Enzyme-linked immunosorbent assay (ELISA) has been developed for fluometuron (Strategic Diagnostics, Inc., Newark, Delaware). This immunoassay is portable, provides rapid results, and is less expensive than conventional methods. Initial analyses have shown very good correlation between GC/MS and ELISA.

Three general factors are important in defining transport, fate, and toxicity of pesticides in the aquatic environment (fig. 5). Pesticide usage, such as illustrated in figures 2 and 3, provides basic sources information. Chemical structure affects the physical properties and, thus, the persistence and mobility of the pesticides. Site hydrology determines runoff and leaching potentials. Evaluation of all factors will enable improved understanding of the processes of nonpoint-source contamination and of the occurrence of cotton pesticides in surface and ground water.

Occurrence of Cotton Pesticides in Surface Water

The major herbicides and their metabolites that have been detected in surface water of the Mississippi Embayment are shown in figure 6. The most-detected compound was fluometuron with a mean concentration of 2.1 µg/L a median of 0.40 µg/L, and a

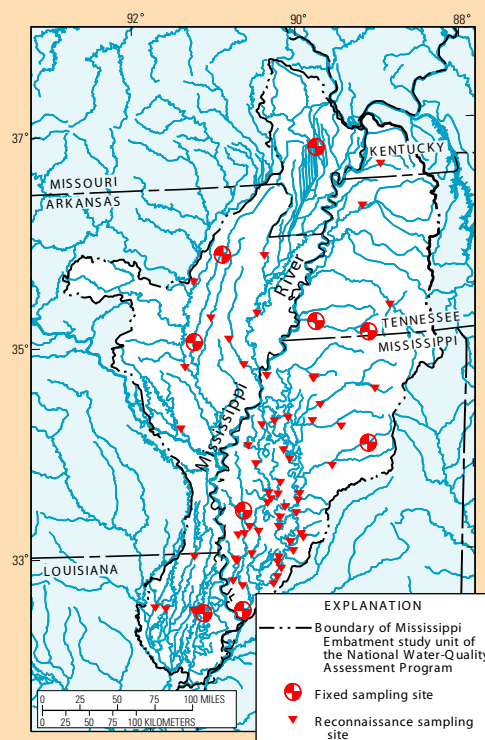


Figure 4. Location of surface-water sampling sites in the Mississippi Embayment.

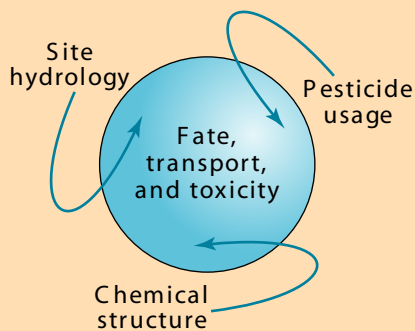


Figure 5. Critical factors affecting the fate, transport, and toxicity of pesticides in the environment.

maximum of 50 µg/L (fig. 6). The demethyl metabolites, demethylfluometuron and demethylnorflurazon, were also commonly detected.

In general, cotton pesticides are slightly soluble in water, from 0.3 to 1,000 mg/L (milligrams per liter). Experience from studies in the corn- and soybean-growing areas of the United States indicates that at a water solubility greater than 5 mg/L compounds are readily carried by surface runoff and occur in surface water. Cyanazine, fluometuron, and norflurazon have water solubilities greater than 5 mg/L. On the other hand, pesticides such as pendimethalin and trifluralin (fig. 3) have a solubility less than 1 mg/L and generally are not detected in surface runoff in the Mississippi Embayment. These low-solubility compounds are tightly bound to soil and are not readily transported to ground water. The pesticide-contaminated soil may be eroded at a later time and may be carried by streams as part of the suspended load along with the pesticides bound to the sediment. Analytical methods are currently (1998) being developed by the USGS to determine how pendimethalin and trifluralin are bound to soil.

The seasonal distribution of total herbicides is shown in figure 7. Cotton has a long growing season, almost 6 months, and herbicides may be applied throughout that period. Total concentrations are highest from May to August when they may reach 100 µg/L. During the nongrowing season, total herbicide concentrations average approximately 11 µg/L.

Insecticides were also detected in the surface water of the Mississippi Embayment, although not as frequently and at much lower concentrations than the herbicides. Figure 8 shows the detections of the insecticides monitored. Dicrotophos was the most frequently detected (35 percent). It is a highly

soluble (1,000 mg/L water solubility) organophosphate insecticide that is used extensively (nearly 0.7 million pounds annually in the cotton-growing areas, see fig. 3). Methyl parathion was detected next most frequently, with 18 percent detections. It is the most-used insecticide in the cotton-growing areas, with more than 3.3 million pounds applied annually (fig. 3). However, because it is a volatile insecticide, it is detected less frequently and at lower concentrations in surface water than dicrotophos, which is much less volatile. The third most-detected compound was profenofos at 12 percent detections. This organophosphate insecticide is used nearly three times as much as dicrotophos, yet it is found in lower concentrations and less frequently. Apparently the shorter half-life of profenofos (about 7 days versus 10 to 15 days for dicrotophos) permits it to be more rapidly decomposed in soil, and as a result, the parent compound occurs less frequently in surface water.

Of the organochlorine insecticides that

were detected (fig. 8), endosulfan was detected most frequently (3 percent) and in the highest concentrations. This result is consistent with the fact that endosulfan is the only organochlorine that is still used legally in cotton-growing areas. Organochlorine insecticides, especially DDT, were used intensively on cotton during past years; therefore, more detailed monitoring by the USGS is underway for DDT and its metabolites using passive sampling methods, such as semipermeable membrane devices (SPMDs). Work with SPMDs shows that DDT and other organochlorine insecticides are present in surface water at detectable levels (Bastian and others, 1997).

Current Research

Additional research by the USGS in the cotton-growing areas includes development of a bacterial-growth assay using the luminescent organism *Vibrio fischeri*. Results from this analytical

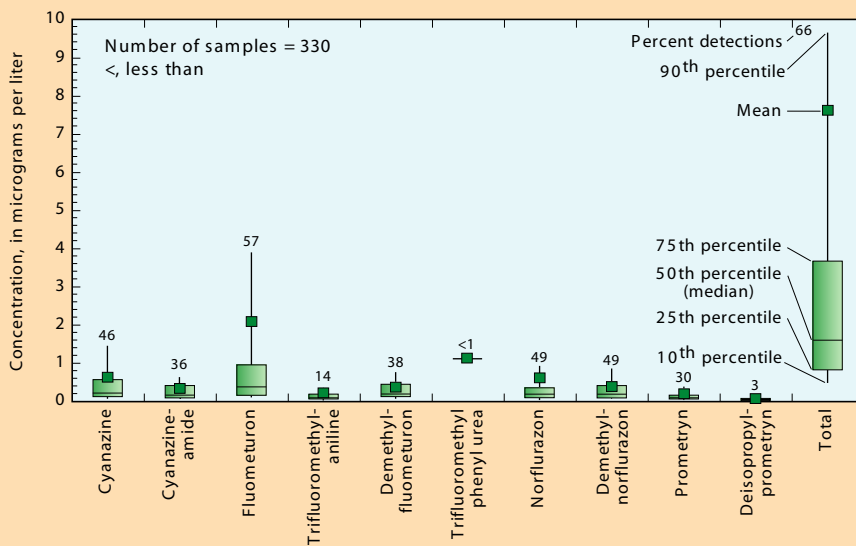


Figure 6. Distribution of detectable concentrations of major cotton herbicides and metabolites in surface-water samples from the Mississippi Embayment, January-December 1996.

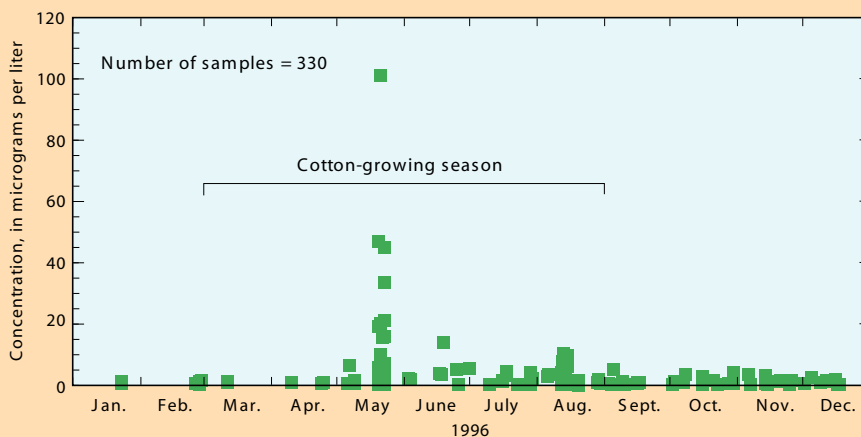


Figure 7. Concentrations of total cotton herbicides in all samples from the Mississippi Embayment, January-December 1996.

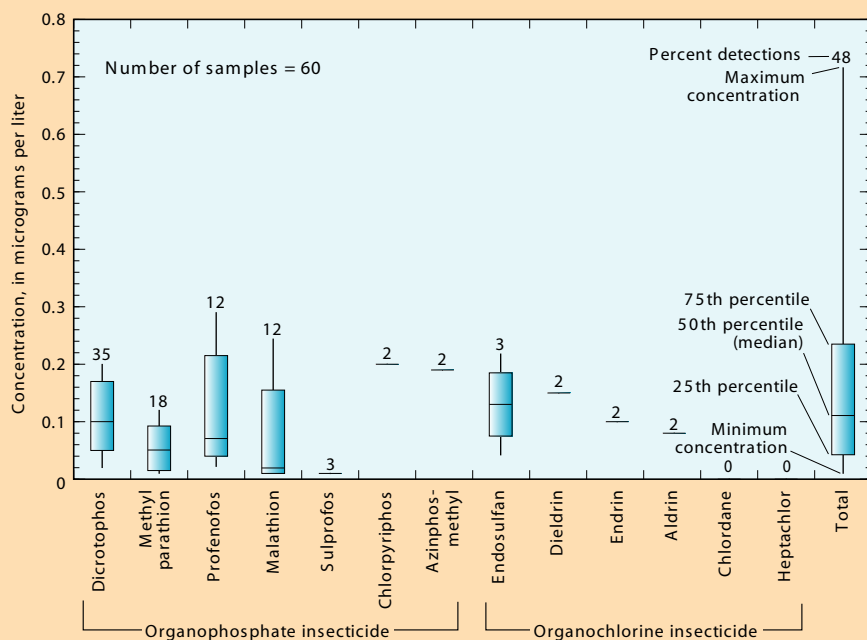


Figure 8. Concentrations of insecticides detected in surface-water samples from the Mississippi Embayment, January-December 1996.

method are being compared with pesticide concentrations determined by chemical analysis to identify the relations among chemical application and spatial and temporal variations in water quality. These bacterial-growth assays also have the potential to identify interactions between the many organic compounds found in surface and ground water of cotton-growing areas.

Also, passive samplers are being tested by the USGS for the determination of some of the most insoluble insecticides, including DDT and its metabolites and the pyrethroids. The passive samplers include SPMDs and SPE disks. These methods are being used on both air and water samples from the Mississippi Embayment.

Methods are also being developed by the USGS using high-performance liquid chromatography/mass spectrometry for the analysis of insecticides and their metabolites. The organophosphorus insecticide metabolites will be analyzed using this method. These metabolites may be mobile in surface and ground water; therefore, methods to analyze these compounds are needed in cotton-growing areas.

Lastly, pesticides in other cotton-growing areas of the United States, including Texas, Arizona, and California, are being examined.

References

- Bastian, K.C., Thurman, E.M., Kleiss, B.A., Coupe, R.H., Jr., Huckins, J.N., and Petty, J.D., 1997, Comparison of pesticide concentrations in semipermeable membrane devices and fish tissue from the Mississippi Delta: Abstract and poster presentation at the 18th Annual Meeting of the Society of Environmental Toxicology and Chemistry, San Francisco, California, November 16-20, 1997.
- Battaglin, W.A., and Goolsby, D.A., 1995, Spatial data in geographic information system format on agricultural chemical use, land use, and cropping practices in the United States: U.S. Geological Survey\X11 Water-Resources Investigations Report 94-4176, 87 p.
- Gianessi, L.P., and Anderson, J.E., 1995, Pesticide use in U.S. crop production- National data report: Washington, D.C., unpaginated.
- Thurman, E.M., Meyer, Michael, Pomes, Michael, Perry, C.A., and Schwab, A.P., 1990, Enzymed-linked immunosorbent assay compared to gas chromatography/mass spectrometry for the determination of triazine herbicides in water: *Analytical Chemistry*, v. 62, p. 2043-2048.

Acknowledgments

Richard Rebich, Mississippi Delta Management Systems Evaluation Areas, Jackson, MS; Dr. David Shaw, Mississippi State University, Starkville, MS; Jim Huckins, Biological Resources Division of USGS, Columbia, MO; and Betsy Beal, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, D.C.

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