DETECTION OF PERSISTENT ORGANIC POLLUTANTS IN THE MISSISSIPPI DELTA USING SEMIPERMEABLE MEMBRANE DEVICES

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INTRODUCTION

Cotton is farmed intensively in the Mississippi River Delta, and pesticide use throughout the past several decades has been similarly intense. Many pesticides, especially those used prior to widespread environmental concerns, are long-lived and very hydrophobic. These tendencies cause the compounds to bioconcentrate in the fatty tissues of fish and other organisms. Many of these compounds can be classified as persistent organic pollutants (POPs). The presence of these pesticides in organisms has potential ramifications not only for the organisms directly affected but also for overall ecological health and for those segments of the human population that depend on subsistence fishing for a significant part of their diet.

Persistent Organic Pollutants (POPs)

POPs are hazardous chemicals, with moderate to low volatility, that resist degradation and tend to accumulate in living tissues. Their persistence in various media facilitates their transport over long distances to remote regions where they have never been used. They have been found to present risks to human health and the environment in polar and other regions (Wahlström 1997). In February 1997, a United Nations Environmental Program Governing Council Decision identified 12 POPs (aldrin, chlordane, DDT, dieldrin, dioxins, endrin, furans, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls, and toxaphene) for which international action was deemed necessary to protect human health and the environment.

Because POPs are present at such low concentrations in the aquatic environment, it is difficult to detect them with conventional chemical analysis, but they still may be important in the environment because they can accumulate in animal fat. Analyzing POPs in water samples is cumbersome because their low solubilities would require large sample volumes to detect concentrations at the levels common in the environment. Fish tissue has been the common method for analysis, but a biological sampling must consider additional complications such as analyte metabolism, disease, predation, migration, or the possible introduction of a foreign species.

Semipermeable Membrane Devices (SPMDs)

SPMDs are devices designed for passive, in-situ monitoring of aquatic contaminants. They consist of a low-density polyethylene (LDPE), lay-flat membrane filled with 1 g (gram) of a high molecular weight lipid, triolein, that cannot diffuse through the membrane. When placed in an aquatic environment, SPMDs passively accumulate hydrophobic organic compounds. The LDPE membrane mimics a biological membrane in its ability to allow selective diffusion of organic compounds. The development and applications of SPMDs have been reviewed recently by Huckins et al. (1996).

The passive sampling of the hydrophobic organic chemicals is driven by lipid-water partitioning. Lipid-containing SPMDs have been used in several environmental settings (Huckins et al. 1990; Lebo et al. 1992; Prest et al. 1992), and their ability to concentrate trace levels of persistent and biodegradable organic contaminants has been demonstrated. Figure 1 shows a cross section of an SPMD deployed in an aqueous environment and illustrates the principals of SPMD sampling. The membrane transport corridor of the SPMD is winding and less than 1 nm (nanometer) in diameter. This prevents losses of the triolein to the environment yet allows permeation of smaller analyte molecules (Huckins et al. 1993). After the deployment period, the SPMDs can be retrieved from the stream, dialyzed, cleaned up with gel permeation chromatography and silica gel, and analyzed using chromatographic techniques.

A close correlation exists between the organic compound's equilibrium triolein-water partition coefficient (K_{tw}) and its respective equilibrium octanol-water partition coefficients (K_{ow}). A compound's K_{tw} should closely approximate its K_{ow} (Chiou 1985). Because log K_{ow} values are large for POPs (greater than 5), the capacity of triolein-containing SPMDs for POPs is high.

Soil half-life and other factors such as intensity of use, application methods, and climatic conditions are important in determining POP transport in surface water. Most of the older "first generation" chlorinated insecticides, such as chlordane, DDT, and dieldrin, are insoluble in water, have long soil half-lives, and large K_{oc} values. Consequently, they are transported primarily on sediment particles. Most of these first-generation chlorinated insecticides are banned and are no longer used in the United States, but they continue to persist in the Mississippi River Basin from previous use on cotton and because of their long soil half-lives. Also, because these chlorinated insecticides are relatively insoluble in water and have large Koc values, they partition into the organic coatings of sediment or accumulate in the fatty tissues of fish and other stream biota (Moore and Ramamoorthy 1984), which is not true for most other pesticides currently in use. Detections of selected POPs and other pesticides in part of the Mississippi Delta using semipermeable membrane devices (SPMDs) is described in this paper.

MATERIALS AND METHODS

Sampling Locations

SPMDs were deployed at five stream sampling sites in the Mississippi Delta for 31 days in June 1996 (Figure 2). The stream sampling sites were the Big Sunflower River at Anguilla, Mississippi (Site 1); Bogue Phalia at Leland, Mississippi (Site 2); Cassidy Bayou at Sumner, Mississippi (Site 3); Steele Bayou near Rolling Fork, Mississippi (Site 4); and the Yazoo River at Long Lake, Mississippi (Site 5). These streams are in the sparsely populated Yazoo River Basin, Mississippi's largest river basin, which consists of about 34,000 km^2 (square kilometers). In May and July 1997, SPMDs were deployed at only the Big Sunflower River near Anguilla, Mississippi (Site 1); Bogue Phalia at Leland, Mississippi (Site 2); and Steele Bayou near Rolling Fork, Mississippi (Site 4).

Sample Apparatus and Collection

SPMDs were acquired from Environmental Sampling Technologies (EST) of St. Joseph, Missouri. A total of 55 SPMDs were prepared for this study. Each SPMD consisted of a 81.4- x 2.54-cm (centimeter) strip of low-density, nonporous polyethylene tubing filled with 1 mL (milliliter) of purified (98 percent) triolein.

At each sampling site, the SPMDs were removed from their protective canisters and placed in stainless-steel deployment devices. A cylindrical deployment device of 0.32-cm stainless mesh with a center post for stacking the SPMD "spider" carriers was used. Each "spider" carrier consists of eight posts in which a single SPMD is woven to provide maximum available surface area for absorption of contaminants as shown in Figure 3. Four SPMDs were placed in each deployment device. Each device was attached to weights to keep it submerged, while floats kept the SPMDs from resting on the bottom of the stream. The sampling sites were located on the downstream side of U.S. Geological Survey (USGS) gaging stations. The SPMDs were deployed in the stream for about 30 days in June 1996, May 1997, and July 1997.

A trip blank was designated for each site and consisted of a sealed canister containing a SPMD. The trip blanks were exposed during deployment to account for any atmospheric contamination of the SPMDs. The trip blank canisters were opened before the other canisters and remained open during the entire deployment period. After the deployment period, the SPMDs were removed from the stream, rinsed of sediment and debris, and shipped back to Environmental Sampling Technologies (EST) of St. Joseph, Missouri. During the recovery of the SPMDs, the trip blanks were re-exposed.

Extraction of Compounds

At Environmental Sampling Technologies, the lipid fraction of each SPMD was removed and combined with other lipid fractions from the same sampling site. Trip blanks were extracted along with the other SPMDs. The extracts were recovered dialytically with a nonpolar solvent, hexane, from the lipid portion of the SPMD. This extract then was reduced, cleaned up, and enriched. The clean-up procedure used gel-permeation chromatography. This process removes any lipid that might have carried over during the dialysis extraction. Further cleanup by enrichment on an activated alumina and silica gel column was done. The enriched extracts were divided, and aliquots were analyzed, using chromatographic techniques, by the USGS National Water-Quality Laboratory (NWQL) in Arvada, Colorado; Environmental Sampling Technologies of St. Joseph, Missouri; and the USGS laboratory in Lawrence, Kansas.

Chromatographic Analysis

The NWQL and Environmental Sampling Technologies (EST) laboratories used gas chromatography/electron capture detection (GC/ECD) techniques. At the USGS laboratory in Lawrence, Kansas, gas chromatography/mass spectrometry detection (GC/Mississippi) analysis of the extracts was done using a Hewlett-Packard Model 5890 Series II plus GC interfaced to a 5972 mass selective detector (MSD) (Palo Alto, California). One microliter (1 mL) of each sample was injected in the splitless mode using an

autoinjector. Separation of the compounds was accomplished with a fused-silica capillary column of 5 percent phenyl methyl silicone (Ultra 2) with a film thickness of 0.33 mm (micrometer), 30-m (meter) x 0.2-mm (millimeter) inside diameter (Hewlett Packard, Palo Alto, California) with a 5-m guard column (Supelco, Bellefonte, Pennsylvania). The column temperature was held at 60° C (degrees Celsius) for 1 minute, ramped at 6° C per minute to 200°C, and then ramped at 30°C per minute to 250°C where it was held. Confirmation of the compounds was based on the presence of the molecular ion and two confirming ions, a retention-time match compared to external standards, and correct area ratios of the confirming ions. The compounds analyzed are listed in Table 1.

Trip blanks were analyzed exactly as deployed samples and were used to define contamination of the SPMD concentrations during transportation and handling. Any concentrations detected in trip blanks were subtracted from SPMD concentrations from the stream sampling sites.

The SPMDs used in 1996 were mishandled and sample extract was lost. Because of the low mass of extract available, data from that sampling is qualitative only.

RESULTS AND DISCUSSION

POPs and Other Pesticides Detected

The POPs aldrin, chlordane, DCPA, DDT, dieldrin, endrin, hexachlorobenzenes (HCHs), heptachlor, mirex, nonachlor, and toxaphene were detected using SPMDs at the Mississippi Delta stream-water sampling sites. In addition, two insecticides still in use, the organophosphate chlor-pyriphos and the organochlorine endosulfan, were detected. Figure 4 shows a chromatogram obtained from the Environmental Sampling Technologies (EST) laboratory using GC/ECD for the Big Sunflower River Site (Site 1, Figure 2) in May 1997. In Figures 5, 6, and 7, calculated concentrations in the SPMDs for Big Sunflower (Site 1, Figure 2), Bogue Phalia (Site 2, Figure 2), and Steele Bayou (Site 4, Figure 2) are shown, respectively.

Total POP concentrations varied little by site and sampling time with one exception. The May 1997 SPMDs sampled at Bogue Phalia (Site 2) had a total concentration of detectable POPs much lower than the other sites and sampling times. This difference is most likely due to biofouling of the SPMDs on the exterior of the membranes. Biofouling can act as an impediment to flux across the membrane, thus slowing the effective sampling rate (R_s). This impedance factor is specific to each SPMD at any given point in time. There is potential for quantifying this impedance for a specific deployment by measuring the loss of a surrogate compound (contained within the SPMD) during deployment, but the SPMDs in this study did not contain any permeability reference compounds to act as surrogate standards.

Toxaphene, an insecticide POP consisting of a complex mixture of chlorinated camphenes, was a major source of chromatogram interference in 1996. Toxaphene was not analyzed in the 1997 SPMDs.

SPMDs have some advantages over traditional methods of water sampling. They can be standardized and may be representative of the thermodynamically dissolved organic phase in surface water. They can be deployed for long periods of time (days to months) and used to estimate the time-weighted mean concentrations of the hydrophobic organic compounds in the water body. For a given nonionic organic chemical, a SPMD will effectively sample 0.5 to 10 L/d (liters per day), depending on the chemical's hydrophobicity (as quantified by its water solubility or octanol-water partitioning coefficient (K_{ow}). A compound with log K_{ow} = 6 would need 200 days at a constant water concentration and at an effective sampling rate of 10 L/d to reach 90 percent equilibrium or more. However, during an initial period, the uptake rate into the SPMD is linear and first order (Huckins et al. 1993). The ambient "truly dissolved" water concentration (C_w) in nanograms per liter (ng/L) can be estimated on the basis of concentrations in the SPMD's lipid (C_{spmd}) in nanograms per gram (ng/g), weight of the lipid in the SPDM (Wt_{spmd}, in grams) the fouling factor (f), the effective sampling rate (Rs), and the time of deployment (t) (Moring and Rose 1997):

$$C_w = \frac{C_{spmd} * Wt_{spdm}}{f * R_s * t}, \quad (1)$$

The fouling factor (f) can be largely due to sediment and other material accumulating on the SPMDs or the stainless-steel deployment device. Mississippi Delta streams carry substantial sediment, and biofouling was very obvious on the deployment devices at the time they were retrieved from the streams. Unfortunately, biofouling hinders the accuracy of SPMDs to indicate water concentrations unless an accurate fouling factor is determined. In this study, permeability reference compounds, which can be used to determine the extent of fouling, were not used. The effective sampling rate (R_s) of many hydrophobic compounds have already

been determined, and more research is underway to expand the number of compounds.

Two herbicides not commonly detected in surface water, pendimethalin and trifluralin, were detected in some SPMD extracts. These two substituted-aniline herbicides are used extensively on cotton and other crops in the sampling basins (Gianessi and Anderson 1995) but have been detected in surface-water samples only at very low concentrations (less than 0.1 mg/L) (Dayama and Coupe 1997; Thurman et al. 1998). Considering their extensive use, the lack of pendimethalin and trifluralin detections in surface-water samples can be attributed to the low solubility (less than 1 mg/L) of these herbicides in water.

Comparison of SPMD Data to Fish-Tissue Data

Previously, fish tissue has been collected at sites within the Yazoo River Basin by State and Federal agencies (Mississippi Bureau of Pollution Control 1984; Schmitt et al. 1990; Plunkett et al. 1997). These data have shown that total DDT concentrations in the fish tissue collected from sites within the Yazoo River Basin are among the highest found in the United States. Kleiss and Justus (1997) provided fish-tissue analysis from tissue samples collected during the fall of 1995 and 1996 at the SPMD sampling sites (Figure 2). A tissue sample consisted of an eight-fish whole-fish composite of common carp (*Cyprinus carpio*) for organochlorine analysis. Figure 7 shows comparisons of the SPMD data to the fish-tissue data for DDT and its metabolites.

Concentrations of DDT and its metabolites detected in SPMD extracts were approximately 1,000 times smaller than those measured in fish tissues (Figure 8). If SPMD data can be corrected for fouling, SPMDs may provide first approximation of concentration of POPs in Mississippi Delta stream. Calculation of water concentrations from SPMD concentration may be possible, although potentially problematic.

CONCLUSIONS

The POPs aldrin, chlordane, DCPA, DDT, dieldrin, endrin, hexachlorobenzenes, heptachlor, mirex, nonachlor, and toxaphene were detected at stream sampling sites within the Cotton Belt using SPMDs. In addition, two insecticides still in use, the organophosphate chlorpyriphos and the organochlorine endosulfan, were detected. These results, along with comparisons to fish-tissue data, suggest that SPMDs can provide an effective first approximation of biological accumulation of POPs in Mississippi Delta water when fouling factors are used. An unexpected finding was that two low-solubility herbicides not detected commonly in surface water, pendimethalin and trifluralin, were sequestered by SPMDs.

ACKNOWLEDGEMENTS

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REFERENCES

Chiou, C.T. 1985. Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. Environmental Science and Technology. 19(1):57-62.

Dayama, Anubha, and R.H. Coupe, Jr. 1997. Pesticides in the Yazoo River and Bogue Phalia, February through September 1996. In Proceedings of the 27th Mississippi Water Resources Conference, March 25-26, 1997, edited by B. Jean Daniel, Mississippi Water Resources Research Institute. 127-132.

Gianessi, L.P., and J.E. Anderson. 1995. Pesticide Use in U.S. Crop Production - National Data Report: Washington, D.C.:National Center for Food and Agricultural Policy.

Huckins, J.N., G.K. Manuweera, J.D. Petty, D. Mackay, and J.A. Lebo. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environmental Science and Technology. 27(12):2489-2496.

Huckins, J. N., J. D. Petty, J. A. Lebo, C.E. Orazio, H. F. Prest, D.E. Tillitt, G.S. Ellis, B.T. Johnson, and G.K. Manuweera. 1996. Semipermeable membrane devices (SPMDs) for the concentration and assessment of bioavailable organic contaminants in aquatic environments, In Techniques in Aquatic Toxicology, edited by G. Ostrander. Boca Raton, FL: CRC - Lewis Publishers. 625-655.

Huckins, J.N., M.W.Tubergen, and G.K. Manuweera. 1990. Semipermeable membrane devices containing model lipid-a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. Chemosphere. 20(5):533-552.

Kleiss, B.A., and B.G. Justus. 1997. Preliminary results of fish tissue analysis in the Mississippi

Embayment NAWQA Program. In Proceedings of the 27th Mississippi Water Resources Conference, March 25-26, 1997, edited by B. Jean Daniel, Mississippi Water Resources Institute, 138-146.

Lebo, J.A., J.L. Zajicek, J.N. Huckins, J.D. Petty, and P.H. Peterman. 1992. Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. Chemosphere. 25(5):697-718.

Mississippi Bureau of Pollution Control. 1984. Ambient Biological Monitoring Report 1983-1984. Jackson, Mississippi.

Moore, J.W., and S. Ramamoorthy. 1984. Organic Chemicals in Natural Waters-Applied Monitoring and Impact Assessment: Springer-Verlag.

Moring, J.B., and D.R. Rose. 1997. Occurrence and concentrations of polycyclic aromatic hydrocarbons in semipermeable membrane devices and dams in three urban stream of the Dallas-Fort Worth metropolitan area, Texas. Chemosphere. 34(3):551-566.

Plunkett, M.L., F. Morris, III, W.T. Oakley, and D.P. Turnipseed. 1997. Mississippi Water Resources Data-Mississippi, Water Year 1996. U.S. Geological Survey Water-Data Report Mississippi-96-01.

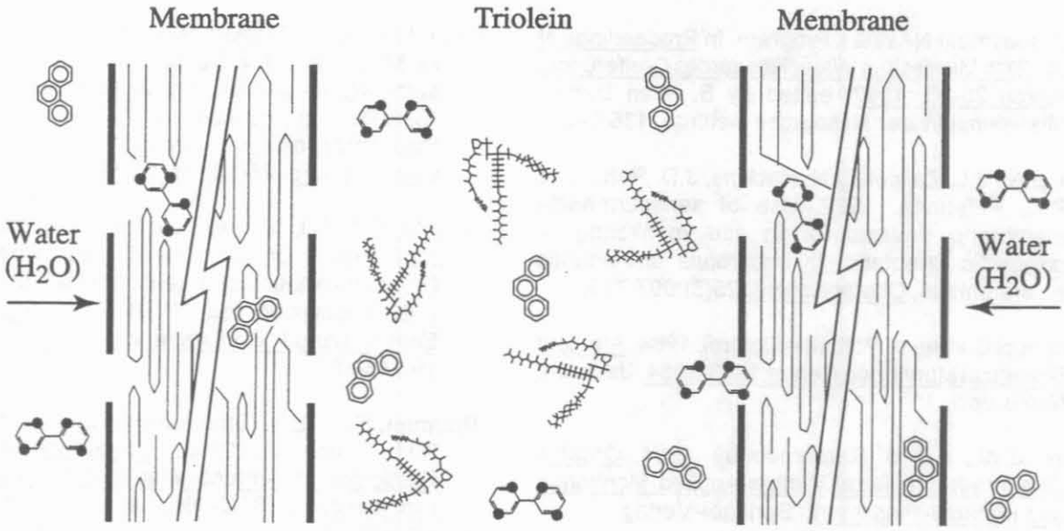
Prest, H.F., W.M. Jarman, S.A. Burns, T. Weismuller, M. Martin, and J.N. Huckins. 1992. Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joaquin River Delta: Chemosphere. 25(12):1811-1823.

Schmitt, C.J., G.L. Zajicek, and P.H. Peterman. 1990. National Contaminant Biomonitoring Program-residues of organochlorine chemicals in U.S. freshwater fish, 1976-1984. Archives of Environmental Contamination and Toxicology. 19:748-781.

Thurman, E.M., L.R. Zimmerman, E.A. Scribner, and R.H. Coupe, Jr. 1998. Occurrence of Cotton Pesticides in Surface Water of the Mississippi Embayment. U.S. Geological Survey Fact Sheet FS-022-98.

United Nations Environment Programme. 1997. Decisions Adopted by the Governing Council at its Nineteenth Session, February 7, 1997, Nairobi, Kenya. Accessed January 29, 1999, at URL http:irptc.unep.ch/pops/gcpops_e.html

Wahlström, B. 1997. Criteria for Identifying Persistent Organic Pollutants-Proceedings of the Subregional Awareness Raising Workshop on Persistent Organic Pollutants, Bamako, Mali. accessed January 22, 1999, at URL http:irptc.unep.ch/pops/POPs_Inc /Proceedings/Iguazu/SUNDEN.html



Compound	Symbol	Dimensions (nanometers) Length	Diameter
Triolein		2.7	2.8
Phenanthrene		1.2	0.8
2,2',5,5'-Tetrachlorobiphenyl		1.2	0.9

Figure 1. Schematic cross section of a semipermeable membrane device in an aqueous environment (modified from Huckins et al., 1993).

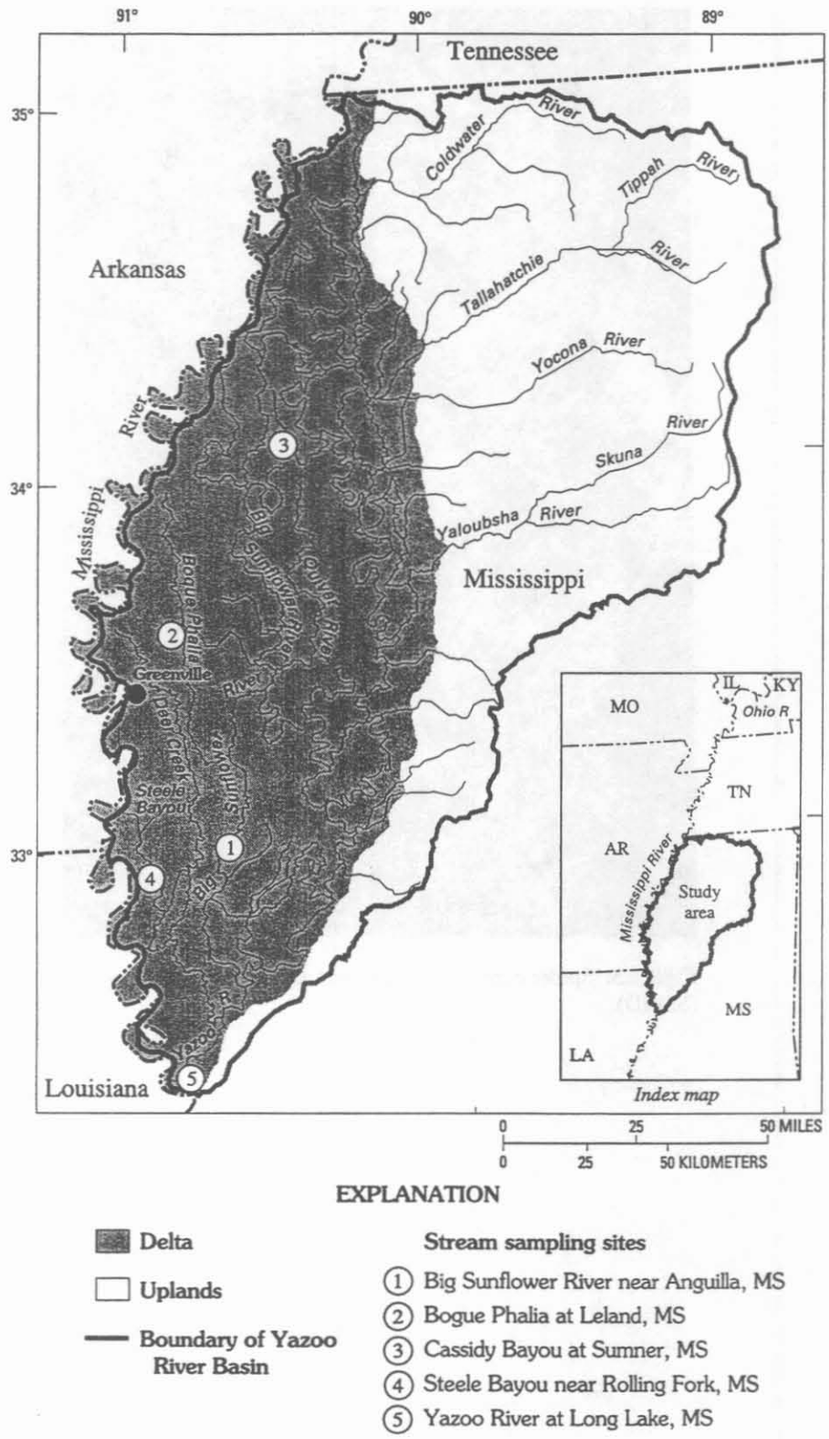


Figure 2. Location of sampling sites in part of the Mississippi Delta.

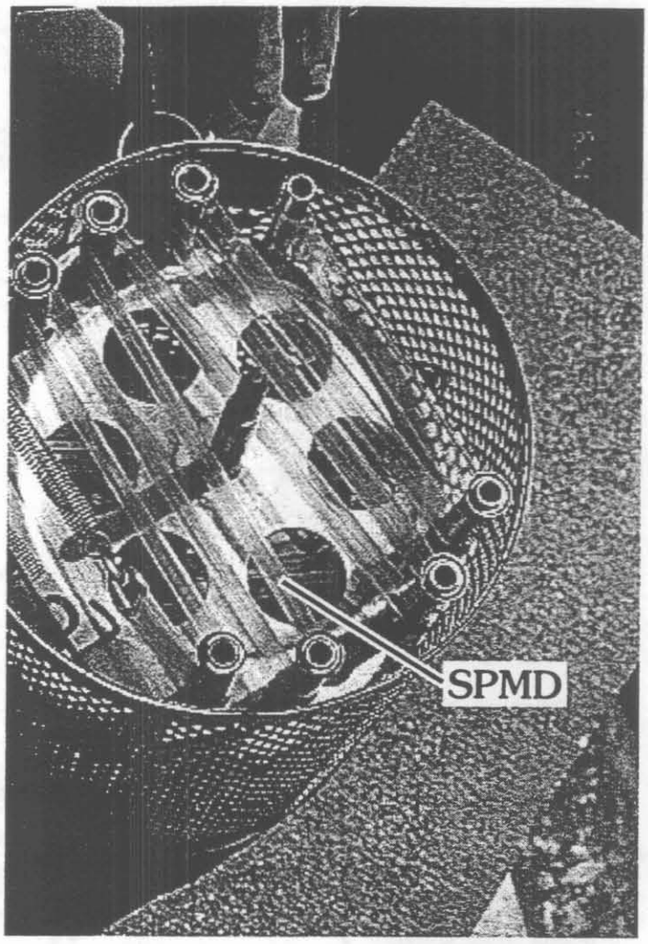


Figure 3. Spider carrier with semipermeable membrane device (SPMD).

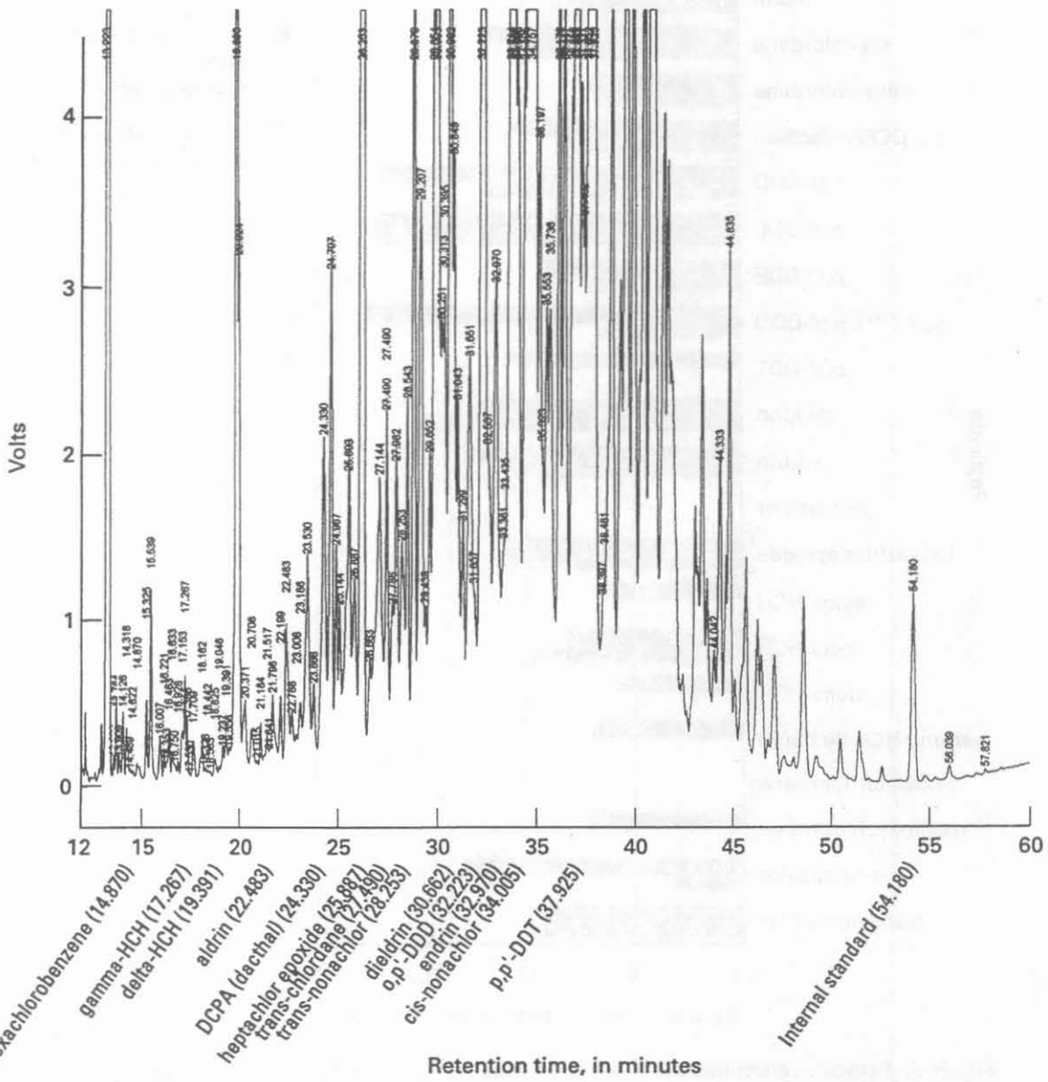


Figure 4. Chromatogram of semipermeable membrane device sample from the Big Sunflower sampling site (site 1, figure 2).

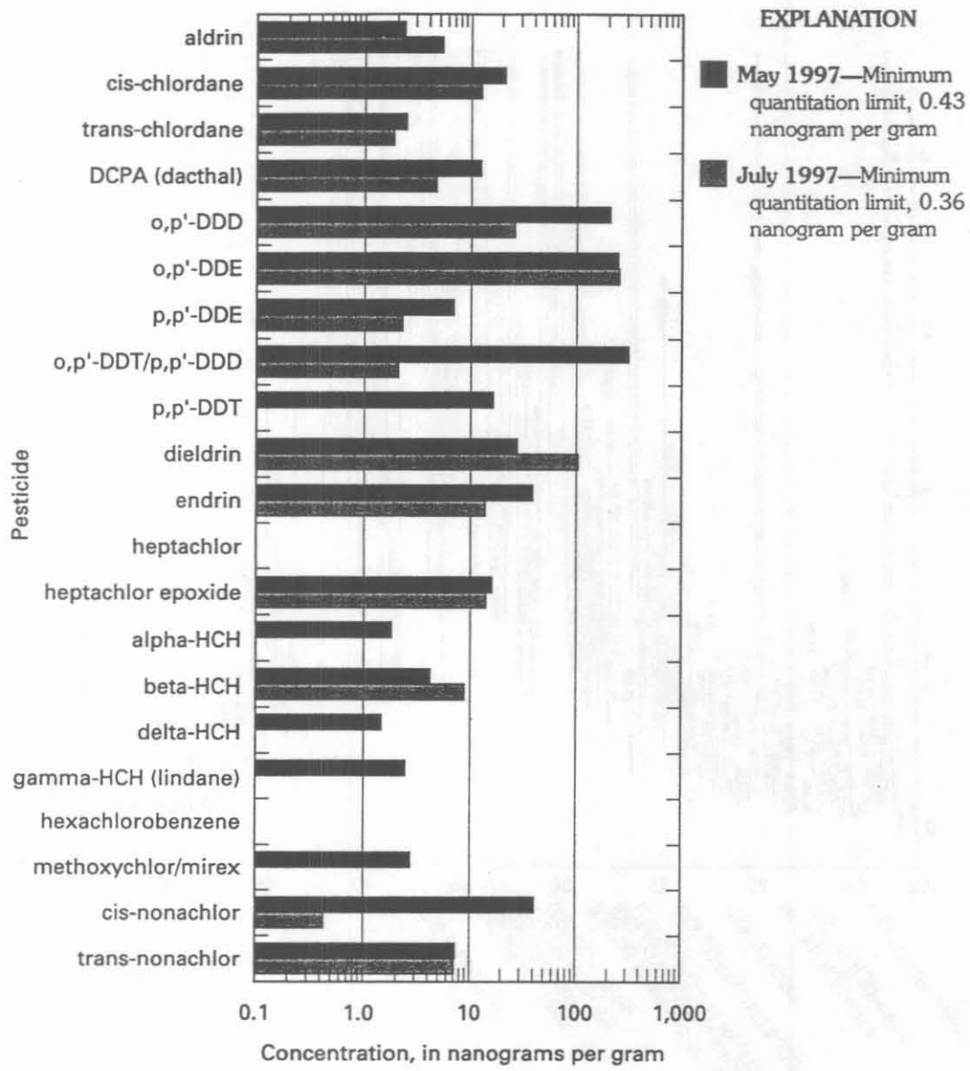


Figure 5. Pesticide concentrations in semipermeable membrane devices at Big Sunflower River sampling site (site 1, figure 2).

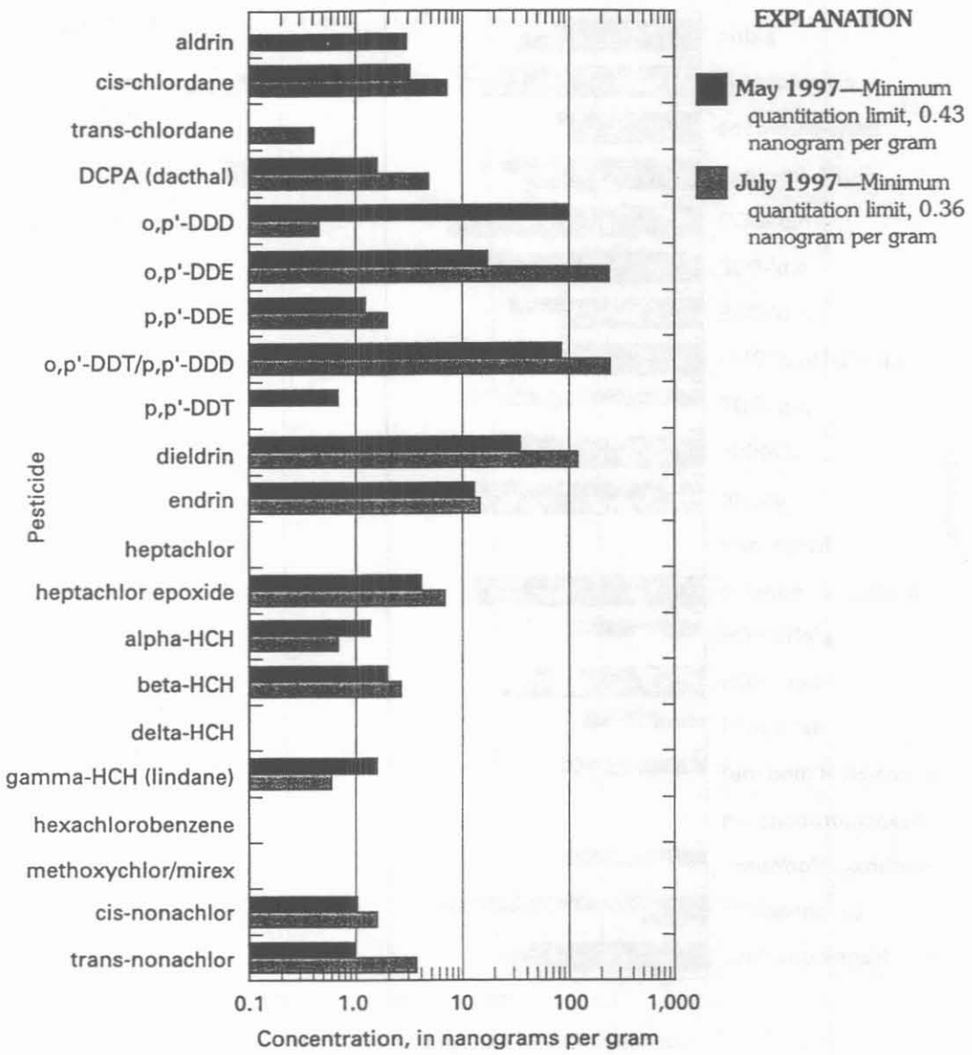


Figure 6. Pesticide concentrations in semipermeable membrane devices at Bogue Phalia sampling site (site 2, figure 2).

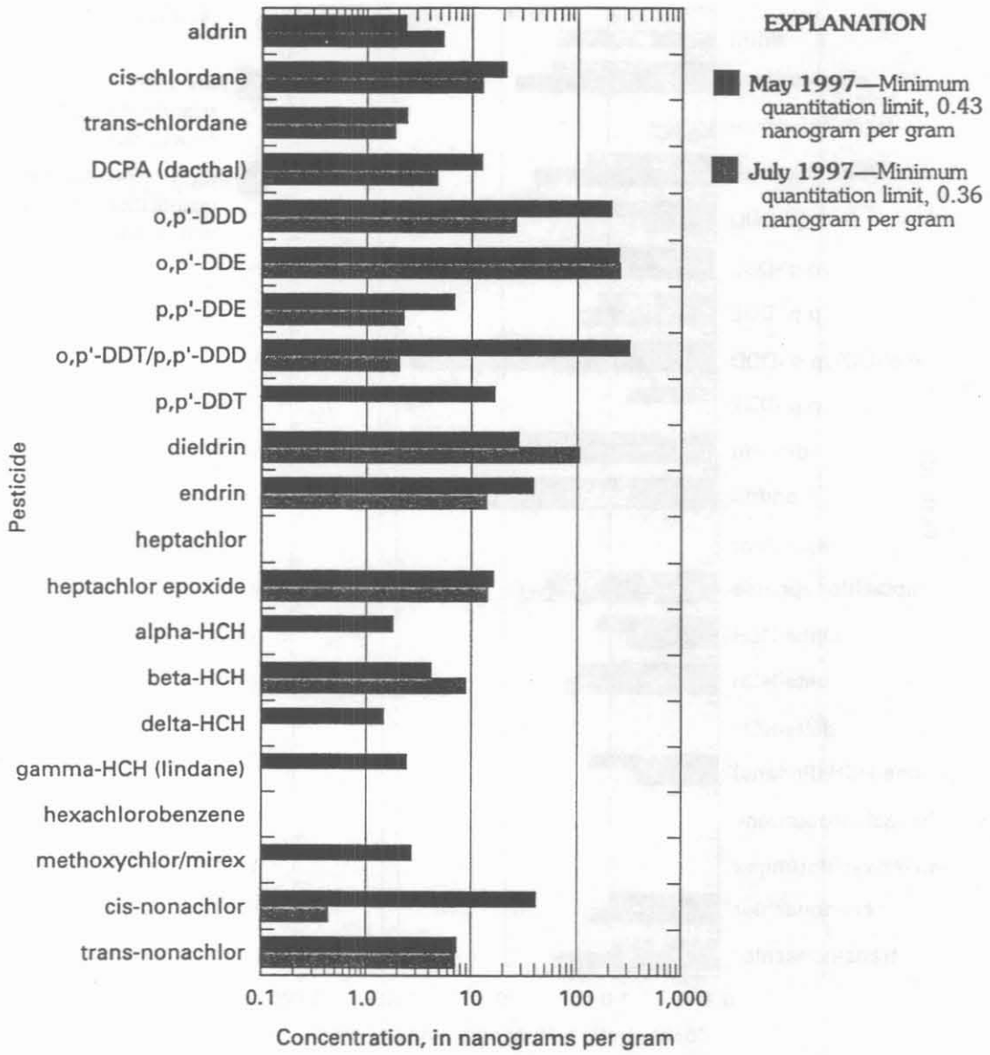


Figure 7. Pesticide concentrations in semipermeable membrane devices at Steele Bayou sampling site (site 4, figure 2).

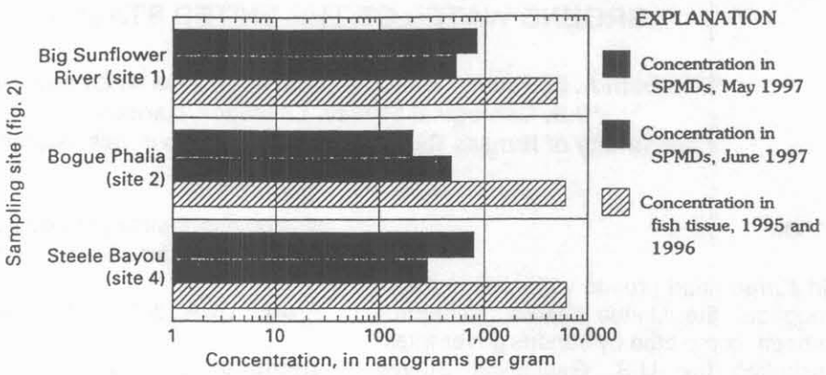


Figure 8. Comparison of semipermeable membrane device (SPMD) data with fish-tissue data for DDT and its metabolites.

Table 1. Pesticide class, compound name, and analysis type for compounds analyzed from semipermeable membrane devices

[IGR, insect growth regulator; OC, organochlorine, OP, organophosphate; Py, pyrethroid, SA, substituted analine]

Pesticide class	Compound name	Analysis type	Pesticide class	Compound name	Analysis type
IGR	methoprene	qualified	OC	nonachlor	qualified
None recognized	DCPA dacthal	quantified	Do.	o,p'-DDD	quantified
OC	aldrin	Do.	Do.	o,p'-DDD	Do.
Do.	alpha-HCH	Do.	Do.	o,p'-DDT	Do.
Do.	beta-HCH	Do.	Do.	p,p'-DDD	Do.
Do.	delta-HCH	Do.	Do.	p,p'-DDE	Do.
Do.	gamma-HCH (lindane)	Do.	Do.	p,p'-DDT	Do.
Do.	cis-chlordane	Do.	Do.	toxaphene	qualified
Do.	trans-chlordane	Do.	OP	azinphos-methyl	Do.
Do.	cis-nonachlor	qualified	Do.	chlorpyriphos	Do.
Do.	trans-nonachlor	quantified	Do.	dicrotophos	Do.
Do.	dieldrin	Do.	Do.	fonofos	Do.
Do.	endosulfan	Do.	Do.	malathion	Do.
Do.	endosulfan II	qualified	Do.	methyl parathion	Do.
Do.	endosulfan sulfate	Do.	Do.	profenofos	Do.
Do.	endrin	Do.	Do.	sulprofos	Do.
Do.	endrin aldehyde	Do.	Do.	terbufos	Do.
Do.	heptachlor	quantified	Py	bifinthrin	Do.
Do.	heptachlor epoxide	Do.	Do.	cyfluthrin	Do.
Do.	hexachloroben-zene	Do.	Do.	cypermethrin	Do.
Do.	methoxychlor I	qualified	Do.	lambda-cyhalothrin	Do.
Do.	methoxychlor II	Do.	Do.	permethrin	Do.
Do.	methoxychlor/ mirex	quantified	SA	pendimethalin	Do.
			Do.	trifluralin	Do.