Evaluation of the use of Semipermeable Polymeric Membrane Devices (SPMDs) for the purpose of monitoring pesticides residues in water

by

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Signatures have been redacted for privacy

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DEDICATION

To my mother, Lois; father, Edward;

daughter, Melissa;

and

my son, Jason

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CHAPTER 1. INTRODUCTION

Preamble

The water quality of our lakes, streams and drinking supplies is a major public concern today, not only in this country but worldwide. Increasingly, people are demanding that our water resources be safe for consumption and recreational use, and that all water resources be maintained in a state that produces no adverse effects to the environment. To protect water quality, a constant vigilance must be maintained over our water resources to monitor the degree of contamination by industrial chemicals and solvents, biological agents and agricultural chemicals, such as pesticides and fertilizers. In addition, we must protect our waterways from particulate pollution as a result of erosion and farm runoff. Here in Iowa, and in other agricultural areas of the world, contamination of water resources by pesticides remains a primary concern.

In Iowa, large quantities of pesticides are being used annually for agricultural purposes, lawn care, mosquito control and various other uses. In 1990, 95% of the 12.8 million acres of corn planted were treated with herbicides, and 35% were treated with insecticides. Of the 8 million acres of soybeans planted, 97% were treated with herbicides and 0.4% were treated with insecticides (Iowa State University Extension, 1991). These figures are given in Appendix 1. In 1990, application of the thirteen major herbicides used in Iowa corn production amounted to 39.4 million pounds of active ingredient (a.i.), with metolachlor being the most heavily used herbicide at 9.4 million pounds (a.i.) (See Appendix 2). On an acreage basis, atrazine was the most popular herbicide, being used on 61% of the acres of corn. The major herbicides applied to soybeans amounted to 10 million pounds (a.i.) (See Appendix 3). Insecticides use on corn amounted to another 4.8

million pounds (See Appendix 4). Trifluralin (3.6 million pounds a.i.) was the major herbicide used on soybeans and terbufos (2.6 million pounds a.i.) was the major insecticide used on corn (Iowa State University Extension, 1991).

In addition to the large quantities of pesticides used in agriculture in Iowa, significant quantities of pesticides were applied for lawn care. In 1990, the golf courses alone in Iowa applied 54,000 pounds of fungicides (a.i.), 81,000 pounds of herbicides (a.i.) and 9,000 pounds of insecticides (a.i) (Iowa State University Extension Golf Course Survery, 1991). The major applied herbicide was 2, 4-D (34,000 pounds a.i.) and the major applied insecticide was carbaryl (653 pounds a.i.). The major applied fungicide was chlorothalonil (5,895 pounds a.i.)

Studies of the Mississippi River drainage area (Gianessi and Puffer, 1990) indicated that more than 294 million pounds of herbicides (a.i.) were used annually during 1987 to 1989 in the twelve states that drain into the Mississippi River (Arkansas, Illinois, Indiana, Iowa, Kansas, Louisiana, Minnesota, Mississippi, Missouri, Nebraska, Ohio, and Wisconsin). Herbicides used in these states account for 60 percent of the total herbicides used in agriculture in the United States. Five herbicides: alachlor (Lasso), atrazine, metolachlor (Dual), EPTC (Eradicaine) and cyanazine (Bladex) accounted for about 63 percent of the herbicides used in this twelve state region in 1987 to 1989.

Pesticides find their way into our lakes and water supplies through several mechanisms (Pionke and Chesters, 1973; Robinson, 1973; Ricci, 1982):

1. direct application
2. atmospheric processes resulting from volatilization and wind erosion
3. seepage in ground water
4. run-off in solutions or as soil-pesticide complex.

Studies conducted by the U.S. Geological Survey in 1989 and 1990 indicate that herbicides are flushed from cropland each spring and summer and are transported into tributaries of the Missouri, Ohio, and Mississippi Rivers (Goolsby et al., 1991b; Thurman et al., 1991). Water testing conducted in the Mississippi River basin in the Spring of 1991 found atrazine present in every one of the 146 samples tested from eight different sites. Metolachlor was found in 98% of the samples, cyanazine in 78%, alachlor in 84%, and simazine in 49% of the samples tested (Goolsby, et al., 1991a).

A study of herbicides in precipitation showed herbicides to be present in precipitation throughout the midwestern and northeastern United States during the late spring and summer of 1990 and 1991 (Goolsby et al., 1993c). During May and June, atrazine, alachlor or both were detected in 60 to 75% of weekly accumulations of precipitation collected at 81 samplings sites in 23 states. Atrazine was the most frequently detected herbicide, followed by alachlor, desethylatrazine and metolachlor.

A 1991 well-water survey in Iowa found atrazine or its metabolites in 10.5% of the 68 well sites tested. Also found were metolachlor (8.1%), alachlor (1.8%), metribuzin (3.0%), propachlor (1.8%) and trifluralin (3.5%) (Iowa Department of Natural Resources, 1993). Appendix 5 summarizes their findings. Another well study performed in 1992 on water collected from 101 wells from the Midwest region of the U.S. found herbicides, herbicide metabolites, or insecticides in 62 percent of the wells sampled (Kolpin et al., 1993). In this study, five of the top six compounds were herbicide metabolites; with ESA (Ethane sulfonate alachlor metabolite) being the most common compound found (See Appendix 6).

The large scale use of pesticides in agriculture has resulted in the contamination of many of our surface water supplies. This, in turn, has led to the contamination of our public water supplies which provide most of our drinking water. A survey of public water supplies in Iowa conducted by the Iowa Department of Natural Resources and the University of Iowa Hygienic Lab in the Spring of 1986 (Wnuk, et al., 1987) found pesticides in treated water supplies. In their analysis of water from 33 treated public water supplies, detectable concentrations of one or more of ten commonly used pesticides were found in 30 of these treated public water supplies. Individual pesticides and the number of water supplies in which they were detected were atrazine, 30; cyanazine (Bladex), 26; metolachlor (Dual), 21; alachlor (Lasso), 17; carbofuran (Furadan), 9; metribuzin (Sencor), 4; 2,4-D, 2; and trifluralin (Treflan), butylate (Sutan) and dicamba (Banvel), 1 each (See Appendix 7). Based on their studies of the Iowa public water supplies, the authors made the following conclusions:

1. Most surface waters used as a source for a public water supply are likely to contain one or more pesticide compounds, at the least, during periods of runoff in spring to early summer.
2. Conventional water supply treatment methods are ineffective at removing pesticides.
3. At the least 22% of the state's (Iowa) population using surface water sources for community public water supplies, are now consuming on a periodic basis, one or more pesticide compounds in their drinking water.

This demonstrates the mobility that many of the pesticides used in agriculture possess. This quality results in the movement of these pesticides, like atrazine and metolachlor, from farm fields to surface waters to drinking supplies. However, one must remember that the levels of pesticides transported to and detected in water supplies may be only a small percentage of the actual pesticide applied to a field. A large percentage of the pesticide applied may be degraded by heat , sunlight, chemical or biological reaction or vaporization before it can reach a water supply and contaminate it (Day 1990).

However, considering the large quantities of pesticides being applied annually, it is understandable that there is great concern for pesticide contamination of our water resources. The residues of many pesticides find their way into our fresh water streams, lakes and drinking supplies and may pose a possible danger to humans, aquatic life, and to the environment in general if their concentration exceeds a level considered to be safe for that particular pesticide. To assure that our water resources are not contaminated with unsafe levels of pesticides and other pollutants, it is necessary to monitor our water supplies regularly. This provides us with information as to what pesticides are finding their way into our rivers and water supplies, and allows us to evaluate what potential dangers they may present.

Review of Previous Work with SPMDs

A Semipermeable Polymeric Membrane Device (SPMD) is basically a device in which a solvent or lipid material is enclosed and sealed within a plastic bag or tube. This device is placed in a medium such as air or water. Chemicals in the medium are then transferred by passive diffusion from the medium, through the polymeric membrane, and into the solvent or lipid within the plastic bag. The solvent or lipid tends to absorb and accumulate the chemicals. Later, the chemicals are removed from the lipid or solvent for analysis by extraction or dialysis (Huckins et al., 1989; Meadows et al., 1993). Various materials have been used for the membrane including regenerated cellulose, vinyl chlorides, silicone or silastic, polyvinylidene fluoride, polytetrafluoroethylene, low density polyethylene and polypropylene. Semipermiable Polymeric Membrane Devices are generally divided into two types: those filled with a nonpolar organic solvent and those filled with a lipid material.

Solvent-containing semipermeable polymeric membrane devices (SPMDs) have been used in the past to monitor contaminants in water. Byrne and Aylott patented a device in 1980 that was used to concentrate small nonpolar organic molecules from water (Byrne et al., 1980). This device used a nonpolar organic solvent contained within a membrane. The membranes that they used were made of regenerated cellulose, vinyl chlorides, polyvinylidene fluoride or polytetrafluoroethylene. Sodegren (1987) was the first to use a solvent-filled hydrophilic dialysis bag to monitor nonpolar contaminants in the environment. He used a regenerated cellulose bag filled with hexane. Miere et al. (1977) were the first to use polyethylene film (which is hydrophobic) for dialysis of nonpolar organic contaminants from water into organic solvents. The advantage of using plastic films such as low density polyethylene and polypropylene over the traditional dialysis bags is that they are hydrophobic and more resistant to organic solvents and biodegradation (Huckins et al., 1990). Most of the solvent-filled SPMDs used to monitor environmental contaminants used hexane, cyclohexane, isooctane or octanol as the absorbing solvent inside the membranes. The use of solvent-filled membrane devices provide a means of in situ monitoring of water for contaminants, and they are advantageous because it is relatively easy to analyze for the contaminants that are absorbed by the solvent.

However, membrane structure limits the number of contaminants that can passively diffuse from the aqueous environment, through the membrane, and into the solvent (or lipid) contained within. Non-porous polymers such as low density polyethylene possess cavities or holes in their crystalline structure in a size range of 5 to 10 Angstroms. This size exclusion allows only chemicals of small molecular size, 10A or smaller, to diffuse throughout the membrane.

Unfortunately, the same mechanism which permits the inward flow of contaminants from the surrounding water environment into the solvent contained within the membrane, permits the outward flow (or escape) of solvent from the SPMD into the surrounding water. Most organic solvents are of small molecular weight, and thus the loss of solvent from the SPMD to the aqueous environment can be large over periods of time such as days or weeks. Huckins et al. (1993) suggested that this solvent loss may also retard analyte uptake from SPMDs because chemicals must diffuse against an outward solvent flux. Solvent loss appears to be the biggest drawback of using solvent-filled SPMDs, for it prevents the use of solvent-filled SPMDs in field monitoring over extended periods of time due to significant solvent loss levels. The solvent loss can be reduced or eliminated by the use of polar nonporous membranes such as cellulose (Sodergren, 1987; Johnson, 1991), but this, in turn, results in a reduction in the uptake of the nonpolar chemicals.

Most of the work involving semipermeable membrane devices has been done using lipids in place of solvents as the absorbent material within the membrane. These lipids are usually triglycerides which have large molecular weights (>600

Daltons). Their large size makes their loss through the membrane very minimal over long periods of time. This gives lipid-filled SPMDs a definite advantage over solvent-filled SPMDs for environmental monitoring over extended periods of time.

The development and use of lipids-containing SPMDs was pioneered by James N. Huckins and associates at the U.S. Fish and Wildlife Service in Columbia, Missouri (Huckins et al., 1990). Huckins and his associates showed that a low density "lay flat" polyethylene tube (SPMD) filled with a thin film of model lipid could be used to mimic the bioconcentration of nonpolar organic contaminants by aquatic organisms. Huckins et al. (1990) used lay flat polyethylene tubings (86.4 cm. long) filled with grass carp lipids and others filled with triolein (a triglyceride) to absorb and concentrate organic contaminants from water. They examined the uptake of 2,2',5,5'-tetrachlorobiphenyl (TCB) from water using these lipid-filled SPMDs. They compared their data to the uptake of 2,2',5,5'-TCB from contaminated water by goldfish (Bruggeman et al., 1981) and showed that the uptake of this chemical from water over time (21 days) by the SPMDs and the goldfish was quite similar. Their data and its comparison to goldfish uptake suggested that for the bioconcentration of 2,2',5,5'-TCB by goldfish, lipid containing SPMDs can be configured to approximate the uptake kinetics of this nonpolar contaminant in fish.

In this study, Huckins et al., demonstrated the ability of a SPMD containing grass carp lipid to absorb and concentrate the pesticides mirex and fenvalerate from contaminated water. However, their data revealed that the polyethylene membrane matrix contained a significant portion of the total recovered residues as opposed to the lipid portion. In a 21-day exposure test where the lipid-containing SPMD was exposed to one liter of well water spiked with mirex (2.1 ug/liter) and fenvalerate (2.2 ug/liter) the following percent distribution was determined: for mirex, 30.9%

was concentrated in the lipid, 46.27% in the membrane matrix, and 0.9% on the exterior membrane surface; for fenvalerate, 64.8% was contained in the lipid, 25% in the matrix and 0.43% on the exterior membrane surface. However, for most of the chemicals tested, the larger percentage was found in the lipid fractions.

Lebo et al. (1992) demonstrated that lipid-filled (triolein) SPMDs could be used to monitor aquatic environments for polycyclic aromatic hydrocarbons (PAHs) and aromatic sulfur heterocycles (ASHs). In their testing, SPMDs were used to absorb an array of PAHs including naphthalenes, phenanthrene and pyrene from a contaminated urban creek. They also were successful in recovering the sequestered chemicals from the SPMD by using dialysis and subsequent cleanup steps.

Further use of Huckins' "Model Lipid" method (Huckins et al., 1990) of using SPMDs to simulate the biocencentration of nonpolar organic contaminants by aquatic organisms was made by Prest et al. (1992) when they simultaneously deployed SPMDs and freshwater clams to absorb pesticides and polychlorinated biphenyls (PCBs) from water at sites on the Sacramento and San Joaquin Rivers in California. In this study, both the clams and the triolein-filled SPMDs were shown to be effective in removing or absorbing organochlorine contaminants from water. However, compared on a lipid-normalized basis, "levels of all organochlorines were roughly 10 to 100 times higher in the clams than in the SPMDs". Several factors were given to possibly explain these differences including the possibility that the SPMDs had not reached an equilibrium state, and that this equilibrium may require much more time depending on the structure of the particular analyte and the membrane. Also, heavy biofouling on the surfaces of the membrane devices could have suppressed the uptake of contaminants. Higher levels in clams could also be explained by the fact that clams could also filter and ingest contaminants that are bound to organic carbon particulates in the water. These bound contaminants are not free to diffuse into the SPMD.

In addition to their use for monitoring water, SPMDs have been used to sample air for lipophilic organic contaminants which are present in the vapor phase. Petty et al., (1993) showed that polyethylene SPMDs containing lipid (triolein) could be used to concentrate polychlorinated biphenyl (PCB) residues from air. Their study suggested that SPMDs could be effective in monitoring air for nonpolar contaminants and in some cases could be used as a device to produce a major reduction in airborne contaminant concentrations.

On the basis of their studies using lipid-containing SPMDs for monitoring aquatic environments for non-polar contaminants, Huckins et al., (1992), have developed several models for the estimation of contaminant concentrations in water. Their models are based on the equilibrium triolein-water partition coefficient (K_{tw}) for the particular contaminant. In the situation where the SPMD has reached saturation for a particular analyte an "equilibrium model" is suggested where $C_u=C_t/K_{tw}$) with C_t being the concentration of the analyte in the SPMD triolein and C_u the concentration of the analyte in the water. Calculation of C_t from residues recovered in dialysates can be made by:

$$C_t = A_{md} / (M_t + K_{mt}M_m)$$

where A_{md} is analyte mass in the SPMD dialysate, M_t and M_m are the masses of the triolein and the membrane, and K_{mt} is the distribution coefficient of a contaminant in the membrane and triolein phases.

For contaminants with high K_{tw} 's ($\geq 2x10^4$), Huckins uses kinetic models. Where SPMD uptake kinetics are linear, then a "Linear Model" for concentration in the triolein can be described as

$$C_t = (PK_{mw}\, C_w A_s/VL)\ (t-T_t)$$

where P is the analyte permeability coefficient, K_{mw} is the membrane and water partition coefficient , A_s and L are the membrane surface area and thickness, V is the volume of triolein, and T_t is the lag time for the contaminant transport through the membrane into the triolein and t is exposure time.

Where the SPMD uptake kinetics are non-linear then Huckins used an "exponential model" where

$$C_t = (K_{mw}C_w/K_{mt})\ [1\text{-}\exp(K_{mt}PA_s/VL(T_x\text{-}t))]$$

where T_x is the x-intercept of the model.

These models have been used to give fairly accurate predictions of contaminant concentrations in water using lipid-filled SPMDs when compared with actual measurements of water concentration (Lebo et al., 1992; Huckins, et al., 1993).

Research Purpose and Goals

As a result of the widespread use of a broad range of pesticides in the environment and the resulting contamination of our water resources by these pesticides, it is necessary to continually monitor these water resources to determine the degree of pesticide contamination that is present. Although the current methods of periodic water sampling, followed by laboratory analysis have proven to be effective and accurate, it is important to look at new methods that could have particular advantages over existing methods. One of these methods is the use of solvent-contained Semipermeable Polymeric Membrane Devices as a means of monitoring pesticide contamination in water. Solvent-filled SPMDs could provide several advantages over standard sampling and analysis methods:

1. Standard sampling methods evaluate the concentration of pesticide contaminants present in water only at one point in time, the moment of sampling, whereas, SPMDs can be placed in a lake or stream over extended period of time and could detect episodic contamination events.
2. SPMDs which can be left in a lake or stream over extended periods of time can absorb and accumulate pesticide contaminants. This can make it possible to detect low levels of contaminants which might not be detectable by analyzing a limited volume of water as in standard tests.
3. SPMDs have the potential to decrease clean-up steps and overall analysis time, for they can accumulate pesticide contaminants in the enclosed solvent. Soil particles and contaminants of large molecular size are prevented from diffusing through the membrane. The SPMD acts to perform its own sample clean-up. The solvent in the SPMD containing the pesticides can be removed, dried down, and analyzed with little or no clean-up involved.

The purpose of my research is to look at the feasibility of using Semipermeable Polymeric Membrane Devices to monitor water resources for the presence of pesticides. The major goals of my study are expressed in the following objectives:

1. To evaluate the use of semi-permeable membrane devices as an alternative method for monitoring water for pesticide contamination, with my major emphasis on the use of solvent-filled SPMDs.

2. To determine the effectiveness of solvent filled SPMDs in extracting a broad range of pesticide types including organochlorines, organophosphates, pyrethroids, carbamates and triazines from water.
3. To look at how various parameters such as time, water temperature, solvents, and pesticide physical properties affect the absorption of pesticides by solvent-filled SPMDs.

CHAPTER 2. LABORATORY STUDIES. THE USE OF SOLVENT-CONTAINING SPMDs FOR EXTRACTION OF PESTICIDES FROM WATER

Materials and Equipment

Reagents

Acetic acid, glacial, reagent ACS (Fisher Scientific)

Distilled water

Fluorescamine (Sigma-Aldrich)

Nitrogen gas (Air Products)

Potassium hydroxide, certified (Fisher Scientific)

Solvents:

- Acetonitrile, Omni Solve Pesticide Grade (EM Science)
- Ethanol, reagent, HPLC Grade (Sigma-Aldrich)
- Ethyl acetate, Certified ACS (Fisher Scientific)
- Hexane, Omni Solve Pesticide Grade (EM Science)
- Methanol, Omni Solve Pesticide Grade (EM Science)
- Methylene chloride, Omni Solve Pesticide Grade (EM Science)

Sodium chloride (Fisher Scientific)

Sodium sulfate (Mallinckrodt Chemical Company)

TCBI (2,6, Dichloroquinone - 4 - chloroimide), (Sigma-Aldrich)

Triolein (C-18: [cis] -9), 99% Purity (Sigma-Aldrich)

Equipment

Bag sealer, Deni Freshlock Vacuum Sealer (Keystone Mfg. Co., Inc.)

Beakers, glass, 100 ml and 400 ml

C-18 SPE cartridges, 0.5 gram capacity, (Plastic cartridges purchased from Analtech), (C-18 purchased from Astec)

Cages, metal barred, (12.5 cm wide x 10.0 cm deep x 10.0 cm high)

Filter Paper - Whatman No. 1, 9.0-cm diameter

Flasks, 250-ml Erlenmeyer

Flasks, 10-ml and 100-ml volumetric

Funnels, glass powder, 2-inch diameter

Gas chromatographs (See instruments of analysis)

Glass jars, amber with phenolic lids, 1250-ml capacity
    hgt = 19 cm, diameter = 10 cm, opening diameter 6 cm

Hot plate

Injection syringe, 10 ml, (Hamilton Co.)

Membrane bags, Dow Ziploc^R quart size, 7-inch x 8-inch
    thickness = .00175 inch (44.5 microns)

Polyethylene tubing, lay flat, 2.54 cm width, film
    thickness = 80-um (micron), (Provided by James N. Huckins of the U.S. Fish and Wildlife Service, Columbia, MO 65202, manufactured by Brentwood Plastic Inc. of St. Louis, MO)

Pipettes, glass

Separatory Funnels, 500-ml and 1000-ml

Thermometer (0 degrees to 100 degrees F)

TLC Plates, Whatman KC 18F Reverse Phase, Fluorescent
    treated (P.J. Colbert Associates)

Tubes, 15-ml volumetric

Pesticide Standards and Spikes

All pesticide standards used in my tests were analytical or technical grade standards. A list of all pesticide standards, with purity and suppliers are listed in Appendix 8. Stock solutions of all pesticides were made up at 1.0 ug/ul. All working standards used in quantitation and all spikes were made from the same stock solutions. All pesticide working standards for G.C. analysis used hexane as the injection solvent.

Instruments of Analysis and Quantitation

Analysis of sample extracts for all organochlorine pesticides, alachlor, cyanazine, metolachlor and metribuzin were performed using the following gas chromatographs and the conditions listed:

Shimadzu GC-14A Gas Chromatograph

Detector: ^{63}Ni-electron capture detector (ECD)

Column: 2.5m-glass with a 5-mm outside diameter packed with 1.5% OV17 /1.95%QFI column packing.

Column Temp.: 200°C

Injector Temp.: 250°C

Detector Temp.: 300°C

Carrier Gas: Nitrogen at a flow rate of 45 ml/min.

Packard 421 Gas Chromatograph

Detector: ^{63}Ni-electron capture detector (ECD)

Column: 6-ft. glass with a 1/4-inch outside diameter, packed with 3.2% SE30/4.8%OV210 column packing.

Column Temp.: 190°C

Injector Temp.: 230° C

Detector Temp.: 280°C

Carrier Gas - Nitrogen at a flow rate of 25 ml/min.

Analysis of sample extracts for organophosphate pesticides, atrazine, butylate and EPTC were performed using the following gas chromatographs under the conditions listed:

Shimadzu G.C. 14 A Gas Chromatograph

Detector - flame thermionic detector (FTD) for nitrogen and phosphorous compounds

Column #1 - 2.5m-glass (5 mm O.D.) packed with 1.5% OV17/1.95% QF1 column packing

Column #2 - 2.5m-glass (5 mm O.D.) packed with 3%OV-1 column packing

Column temp.: 200°C (150°C for EPTC and butylate)

Injector temp.: 250°C

Detector temp.: 300°C

Nitrogen carrier gas at a flow rate of 20 ml per minute

Analysis of pyrethroid pesticides was performed on the following gas chromatograph under the conditions listed:

Packard 421 Gas Chromatograph

Detector: ^{63}Ni-electron capture detector (ECD)

Column: 6ft.-glass with a 1/4-inch outside diameter, packed with 3.2%SE30/4.8% OV210 column packing

Column temp.: 250°C

Injector temp.: 230°C

Detector temp.: 280°C

Carrier gas: nitrogen at a flow rate of 25 ml/minute

Determination of pesticide recoveries using gas chromatography was accomplished by comparing peak heights of known standard concentrations to peak heights of sample injections. Pesticides were identified in the samples by comparing retention times of the sample peaks to retention times of known standards. In most cases, a second G.C. system was used for confirmation.

A linear curve was plotted using peak heights of the primary standards containing known quantities of the pesticides of interest. The standard curve was constructed from standards injected at three different known concentrations. All three standard concentrations were injected before and after injections of samples were made, and an average peak height value was determined. This average was used to plot the standard curve. The quantity of pesticide in each sample was derived from the standard curve and calculated in ng/ul of sample solution. This sample concentration was used to determine percent recoveries of the spiked pesticides. Sample recoveries were reported as an average of the two recovery values from the duplicate samples that were analyzed.

Quantitation of carbamate pesticides was made using thin layer chromatography analysis. Known volumes of samples were cleaned up using C-18 SPE cartridges. The samples were then concentrated and spotted on C-18 reverse phase, fluorescent treated, TLC plates (Whatman KC18F TLC plates). Carbamate standards were spotted at ten different concentration levels to create a standard concentration curve. The plates were developed in a glass chamber using ethanol:

H_2O: acetic acid (65:35:1) as the developing solvent. Plates were removed from the chamber, dried, and then sprayed with 10% KOH solution, fluorescamine solution, and TCBI (2,6 dichloroquinone-4-chloromide) solution. Carbaryl and carbofuran developed a bright blue color upon spraying. Thifensulfuron methyl and carboxin developed black spots when viewed under short-wave fluorescent light (at 254 nm). Spot intensity of the samples was compared to spot intensity of the standard concentrations to determine concentration of carbamates in the sample and percent recoveries.

Experimental Procedures and Parameters

The first group of laboratory studies were performed to analyze the effectiveness of solvent-filled SPMDs in the extraction or removal of pesticides from water. A series of tests was set up to determine the capabilities of a solvent-filled SPMD in recovering various groups or families of pesticides from water which had been spiked with a known concentration of these pesticides. The test procedures and parameters were the same for each test, but each was designed to look at a different pesticide family. In all tests, the percent of pesticides absorbed by the solvent within the SPMD was determined. However, Test #1 also measured the actual level of pesticide remaining in the contaminated water at the completion of the test.

The test procedure consisted of adding 1000 ml of tap water to a 1250-ml amber glass jar. The water was then spiked with a known concentration of pesticide at a level of approximately 10 ppb (10,000 ng in 1000 ml of water). A spike level of 10 ppb was chosen because it represents pesticide contaminant levels that are commonly found in the environment. Prior to spiking, the water temperature of all test containers was adjusted to near room temperature at 70°F (21.1°C). The initial water temperature was recorded. Spiking was performed by adding 10 ul of pesticide at a concentration of 1.0 ug/ul with a 10-ul Hamilton injection syringe. Immediately after spiking, the jar was capped and shaken for one minute to disperse the pesticide in the water. Methylene chloride ($MeCl_2$) was chosen as the absorbing solvent placed within the SPMD because of its ability to extract a broad range of pesticide types. One hundred milliliters of $MeCl_2$ were added to the SPMD. The SPMD consisted of a 7-in. by 8-in. low density polyethylene bag with a membrane thickness of .00175 in. or 44.5 um. The bag with the $MeCl_2$ was then submerged into the jar containing the spiked water to a point where the $MeCl_2$ level in the bag was below the water surface level. The top of the plastic bag was draped over the top of the jar, and the jar was then sealed with a plastic phenolic cap.

All samples were run in duplicate and a water blank was run as a control to insure that the tap water did not contain any of the spiked pesticides or produce any peaks on the G.C. that may correspond to the retention times of standard pesticide peaks.

The membrane device was left in place in the water for a period of 24 hours at room temperature. After 24 hours, the membrane device was removed from the water, and the water temperature was again measured and recorded. The $MeCl_2$ was poured from the membrane bag into a 100-ml graduated cylinder and the amount of $MeCl_2$ recovered, per 100 ml initially used, was recorded. The membrane bag was then rinsed with 50 ml of $MeCl_2$ and the rinse was added to the $MeCl_2$ recovered from the bag. The $MeCl_2$ was then transferred to a 250-ml Erlenmeyer flask. The flask was then placed on a hot plate set at low heat, and the $MeCl_2$ was concentrated to 3-4 ml with nitrogen gas. The samples were then quantitatively transferred with $MeCl_2$ to a 15-ml graduated drying tube. Nitrogen was then used to concentrate the sample just to dryness. Hexane was then added to the tube to bring the sample volume up to the desired volume for G.C. analysis. This volume was usually 5 or 10 ml, depending on the pesticide and its G.C. sensitivity. A quantitation was then made to determine pesticide concentration and percent recovery in the SPMD.

Test 1. Recovery of Aldrin, Atrazine and Chlorpyrifos

In the first test, the recoveries of aldrin, an organochlorine insecticide, atrazine, a triazine herbicide, and chlorpyrifos, a chlorinated organophosphate insecticide were evaluated. The concentration of pesticide dissolved in the $MeCl_2$ within the polyethylene SPMD and the concentration of pesticide remaining in the water fraction were calculated.

The water fraction was extracted using a liquid-liquid extraction method. This is a long-established procedure for the extraction of pesticide from water including triazines and other nitrogen containing herbicides (Wershaw et al., 1987). This procedure is based on the extraction of a one-liter sample of water with $MeCl_2$. The water was extracted once by partitioning with 100 ml of $MeCl_2$, followed by a second extraction with 50 ml of $MeCl_2$. The extracts were combined in a 250-ml Erlenmeyer flask and concentrated for analysis as described previously for the dry-down of the SPMD $MeCl_2$ fraction. The water fraction was then analyzed on G.C. to determine pesticide concentration. The results of the test are summarized in Table 1 and Figure 1.

Review of the results indicates that the $MeCl_2$-filled SPMD is capable of absorbing the three compounds from water to varying degrees over a 24-hour

Table 1. Recovery of Aldrin, Atrazine, and Chlorpyrifos Using a $MeCl_2$-Filled SPMD in a 24 Hour Test

Pesticide	Amount Spiked	Avg. $MeCl_2$ Recovered from SPMD per 100ml	Recovery from $MeCl_2$ in SPMD (%)	Recovery from Water(%)	Percent Pesticide Unrecovered
Aldrin	10.8ppb	75 ml	47.9	4.30	47.8
Atrazine	10.7ppb	78 ml	35.2	54.80	10.0
Chlorpyrifos	10.3ppb	78 ml	73.0	5.50	21.5

exposure period. Absorption of chlorpyrifos was the highest at 73%, followed by aldrin at 47.9% and atrazine at 35.2%. Differing degrees of absorption could be explained by differences in physical characteristics of the three compounds. Water solubility would favor the absorption of aldrin by the $MeCl_2$, since aldrin is practically insoluble in water. Next would be chlorpyrifos whose water solubility is 2 ppm at 25°C and finally, atrazine for which the water solubility is 70 ppm at 25°C (Merck Index. 1989).

The degree of partitioning of the compounds between the water phase and the $MeCl_2$ phase is probably best defined as a relationship between fat solubility and water solubility. Fat soluble or hydrophobic compounds would tend to migrate more readily through the polethylene membrane into the less polar solvent and away from the polar water layer. This relationship can be measured as the octanol-water partition coefficient, Kow, for each compound. This is generally expressed in the form of the logarithm of Kow or log Kow. Higher values of log Kow represent a higher degree of fat solubility as opposed to water solubility. Log Kow for aldrin is 7.4 (Briggs, 1981), for chlorpyrifos, 4.98 (Kenaga and Goring, 1980), and for atrazine, 2.68 (Kenaga and Goring, 1980). Log Kow and water solubility values for

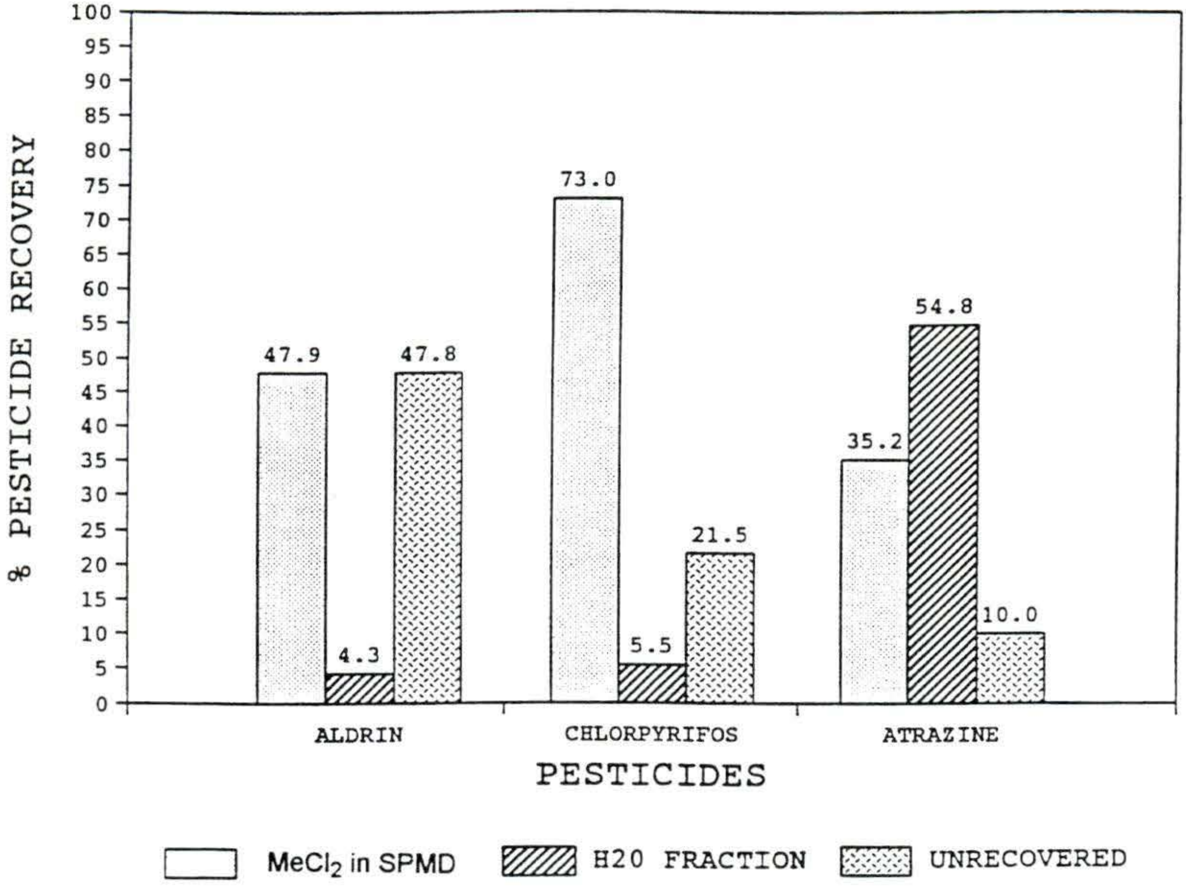

Figure 1. Recovery of aldrin, chlorpyrifos and atrazine from water using a solvent containing semipermeable device

selected pesticides are given in Appendix 9. From these values, aldrin and chlorpyrifos would be expected to have the greater mobility, from the water into the SPMD containing $MeCl_2$. Atrazine, being the most hydrophilic, would be expected to have the least mobility as was supported by the data. Atrazine also shows the highest percentage retained in the water fraction as would be expected from its higher water solubility and lower log Kow value.

The most striking feature of the data is the high amount of aldrin (47.8%) and chlorpyrifos (21.5%) that was unrecovered in either the $MeCl_2$ or water fractions. Small losses could be expected during extraction and dry-down, but not such large losses, especially for aldrin which is very resistant to breakdown and loss through vaporization. The high losses could be explained by the assumption that the polyethylene membrane had absorbed and retained high levels of these compounds, for the membrane itself is nonpolar in nature. Huckins et al. (1990) found that polyethylene membrane matrices of SPMDs contain significant portions of total recovered residues. In a test using lipid-filled SPMDs, they found that 46% of the pesticide mirex and 25% of the pesticide fenvalerate was retained in the polyethylene membrane. This could explain why aldrin, being more nonpolar than chlorpyrifos showed low recovery values in the $MeCl_2$ fraction. Aldrin might be absorbed to a greater degree by the polyethylene membrane than is chlorpyrifos.

Also, in examining the recovery rates of the three compounds, it must be remembered that the exposure time of the test was 24 hours. There is no assurance that an equilibrium state had been reached after 24 hours for the partitioning of the chemicals between the water and solvent fractions. It is possible that higher levels of compounds could be recovered in the $MeCl_2$ of the SPMD if exposure time is extended beyond the 24 hours. The time of equilibrium is different for each compound depending on solubility, molecular size, and diffusion rate.

Test 2. Recovery of Organochlorine and Dinitroaniline Pesticides

In this test, the effectiveness of a solvent-filled SPMD in recovering various chlorinated and dinitroaniline pesticides from water was evaluated. Methylene chloride was used as the test solvent in the membrane device and a 24-hour exposure time was again used. Procedures and parameters for the test were the same as described earlier for Test 1. Results are shown in Figure 2 and experimental data is given in Tables 2A and 2B.

Pesticide recoveries ranged from 26.9% for p,p'-DDE to 86.6% for metolachlor. Metolachlor, propachlor and alachlor are chlorinated amides. Trifluralin and pendimethalin are dinitroaniline herbicides. Recovery for the two dinitroanilines, pendimethalin and trifluralin, are very good at 78.8% and 73.4%. Also, the chlorinated amides, alachlor (85.8%), metolachlor (86.6%) and propachlor (71.3%), showed good recoveries. Recoveries in the $MeCl_2$ fraction of the SPMD for the organochlorine pesticides were much lower than expected, but supported the data reported for aldrin in the first test. Considering the high log Kow values for these organochlorines, they should diffuse well from the polar water fraction to the less polar solvent inside the membrane bag. Once again, one would theorize that the membrane bag itself, being nonpolar, was absorbing large quantities of the pesticides; this resulted in lower recoveries in the $MeCl_2$ fraction. This is similar to the results that Huckins et al. (1990) reported in their recovery of the chlorinated pesticide mirex. Additional tests extracting the plastic membrane and the water

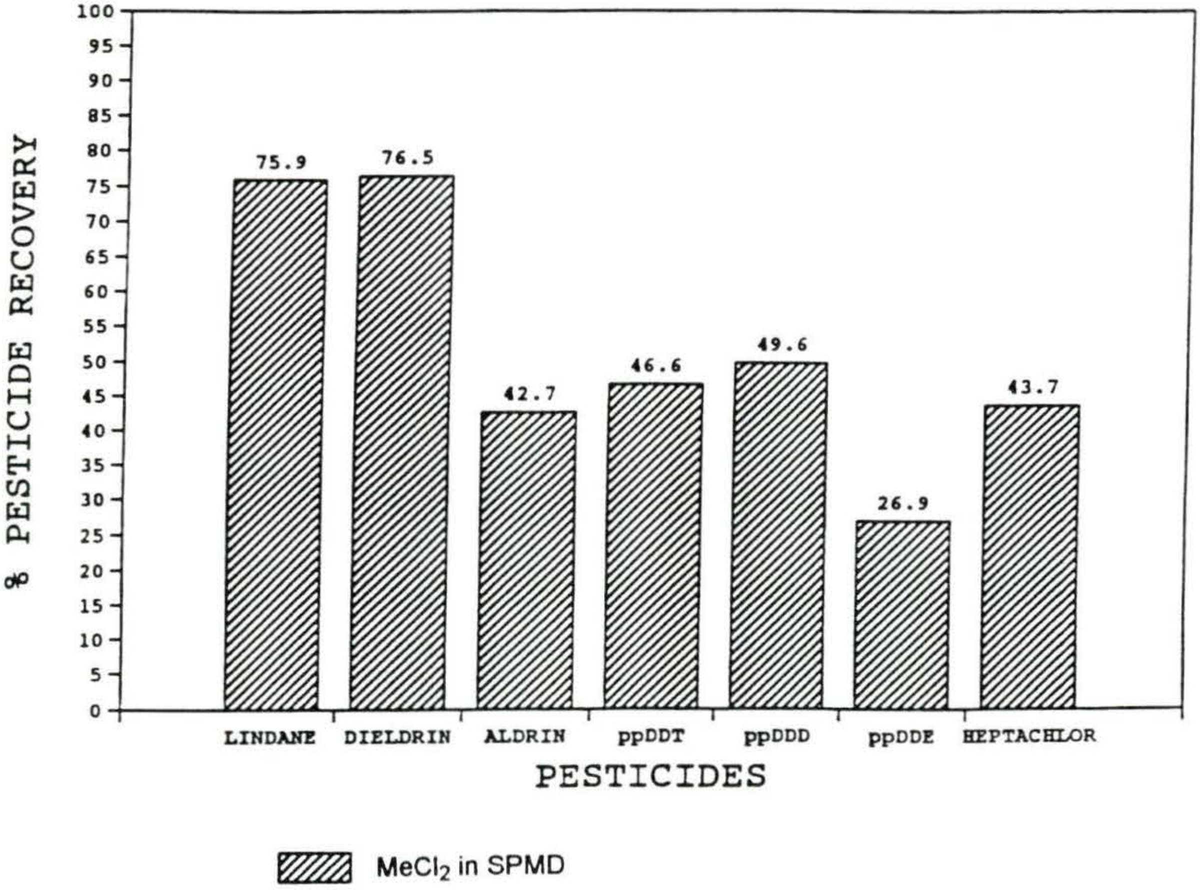

Figure 2. Recovery of chlorinated pesticides and dinitroanilines from water using a solvent containing semipermeable membrane device

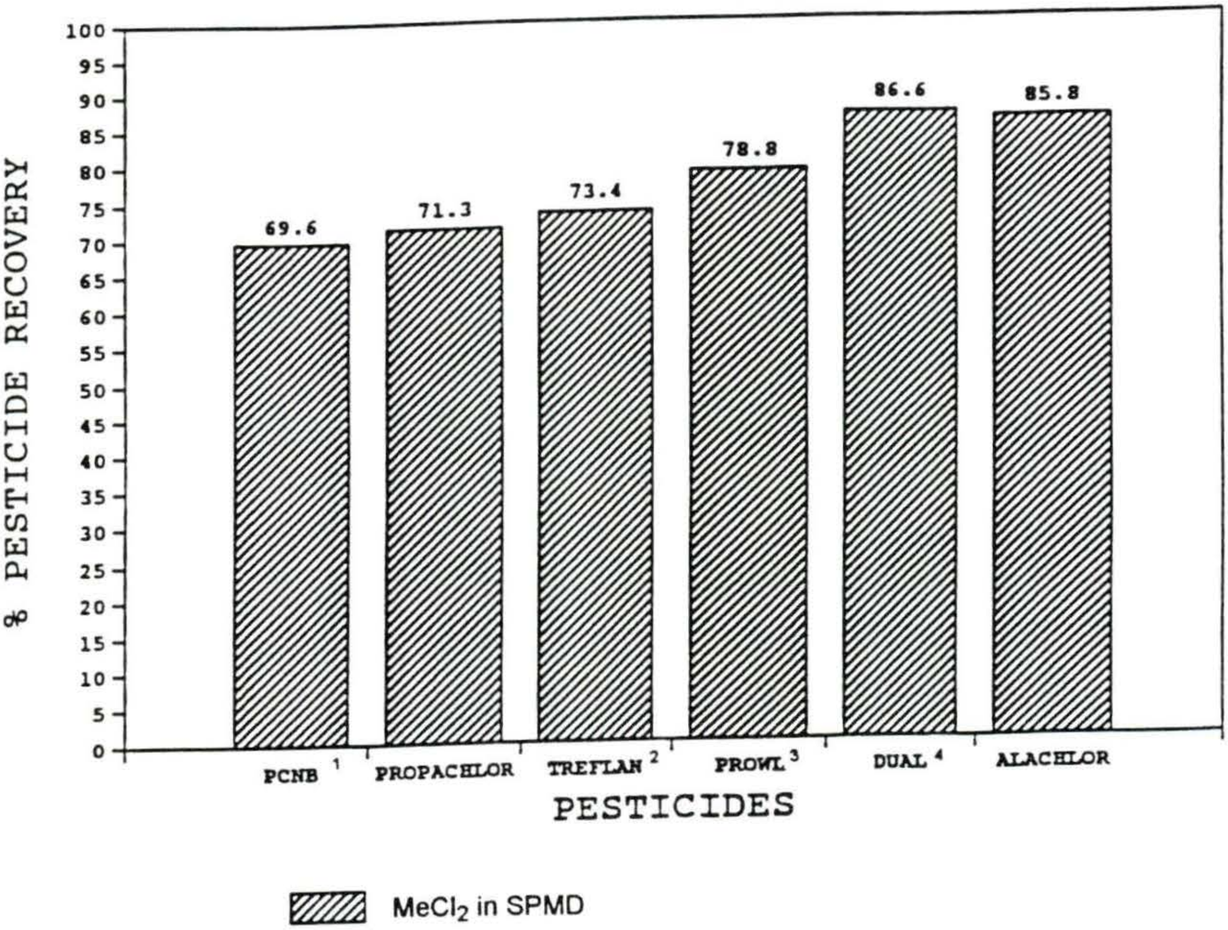

Figure 2. (Continued). [1]Common name is pentachloronitrobenzene, [2]common name is trifluralin, [3]common name is pendimethalin, [4]common name is metolachlor

Table 2. Recovery of Organochlorine and Dinitroaniline Pesticides Using a $MeCl_2$-filled SPMD - 24 Hour Test

A. Physical Test Data

Container #	**Description**	**Recovery of $MeCl_2$ in SPMD per 100 ml**
1	Blank	80 ml
2	Spike 1A	81 ml
3	Spike 1B	82 ml
4	Spike 2A`	82 ml
5	Spike 2B	82 ml

B. Pesticide Recovery Data

Spike	**Pesticide**	**Amount Spiked (ppb)**	**Average % Recovery in $MeCl_2$ Fraction**
1A and 1B	Trifluralin	1.04	73.4
1A and 1B	PCNB	9.90	69.6
1A and 1B	Alachlor	10.70	85.8
1A and 1B	Metolachlor	9.50	86.6
1A and 1B	Pendimethalin	10.20	78.8
1A and 1B	Dieldrin	10.50	76.5
2A and 2B	Propachlor	10.90	71.3
2A and 2B	Lindane	10.50	75.9
2A and 2B	Heptachlor	10.00	43.7
2A and 2B	Aldrin	10.80	42.7
2A and 2B	pp DDE	10.90	26.9
2A and 2B	pp DDD	9.80	49.6
2A and 2B	pp DDT	9.90	46.6

fraction for these organochlorines need to be performed to confirm this theory. It would be expected that very low percentages of the organochlorines would remain in the water for fraction as was shown for aldrin in Test 1.

Test 3. Recovery of Carbamate Pesticides

In this test, recoveries of the carbamate pesticides carbaryl, carbofuran (Furadan), and carboxin were evaluated. Carbaryl and carbofuran are true carbamate insecticides, whereas, carboxin is a carboxamide compound used as a fungicide. Test procedures and parameters are the same as for Tests 1 and 2. Quantitation was performed using thin layer chromatography analysis as described earlier.

The recovery of all three compounds is fairly low in the SPMD. This would be expected when considering their low log Kow values of 2.32 for carbaryl, 1.60 for carbofuran, and 2.17 for carboxin. Experimental test data is given in Table 3A, and pesticide recovery data is given in Table 3B and Figure 3.

Water solubility for carbofuran (700 ppm at 25°C), carbaryl (40 ppm at 25°) and carboxin (170 at 25°C) is significantly greater than for most organochlorines. Considering this higher water solubility, it would be expected that these compounds would be more difficult to partition from the water fraction. See Appendix 9 for water solubility values of selected pesticides.

Table 3. Recovery of Carbamate Pesticides Using $MeCl_2$ filled SPMD in a 24 Hour Test

Table A. Physical Test Data

Container #	**Description**	**Recovery of $MeCl_2$ in SPMD per 100 ml**
1	Blank	77
2	Spike 1A	77
3	Spike 1B	75
4	Spike 2A	80
5	Spike 2B	79
6	Spike 3A	78
7	Spike 3B	78

Table B. Pesticide Recovery Data

Spike	**Pesticide**	**Amount Spiked (ppb)**	**Average Percent Recovery in $MeCl_2$ Fraction**
1A and 1B	Carbofuran	10.0	40%
2A and 2B	Carbaryl	10.0	55%
3A and 3B	Carboxin	10.6	35%

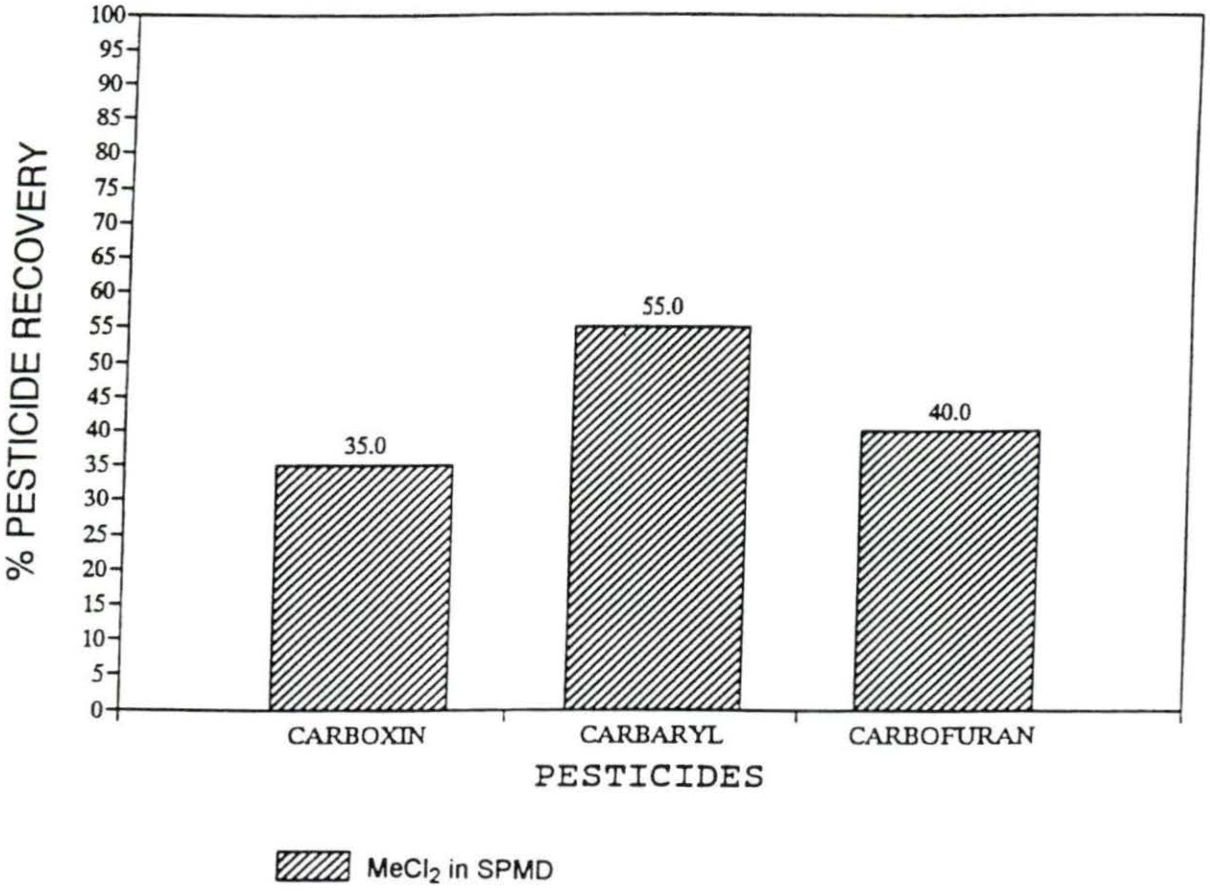

Figure 3. Recovery of carbamate pesticides from water using a solvent-containing semipermeable membrane device

Test 4. Recovery of Pyrethroid Insecticides

In this test the recoveries of the pyrethroid insecticides cis and trans permethrin, flucythrinate, and esfenvalerate were evaluated using the same procedure and parameters as the previous tests. (Esfenvalerate is the most active isomer of the insecticide fenvalerate.) Results are given in Tables 4A and 4B and in Figure 4.

Table 4. Recovery of Pyrethroid Pesticides Using a $MeCl_2$-Filled SPMD in a 24 Hour Test

Table A. Physical Test Data

Container #	**Description**	**Recovery of $MeCl_2$ in SPMD per 100 ml**
1	Blank	80
2	Spike 1A	80
3	Spike 1B	81

Table B. Pesticide Recovery Data

Spike	**Pesticide**	**Amount Spiked**	**Average Percent Recovery in the $MeCl_2$ Fraction**
1A and 1B	cis-Permethrin	10.0 ppb	22.3
1A and 1B	trans-Permethrin	10.0 ppb	21.8
1A and 1B	Flucythrinate	10.3 ppb	23.4
1A and 1B	Esfenvalerate	10.8 ppb	16.3

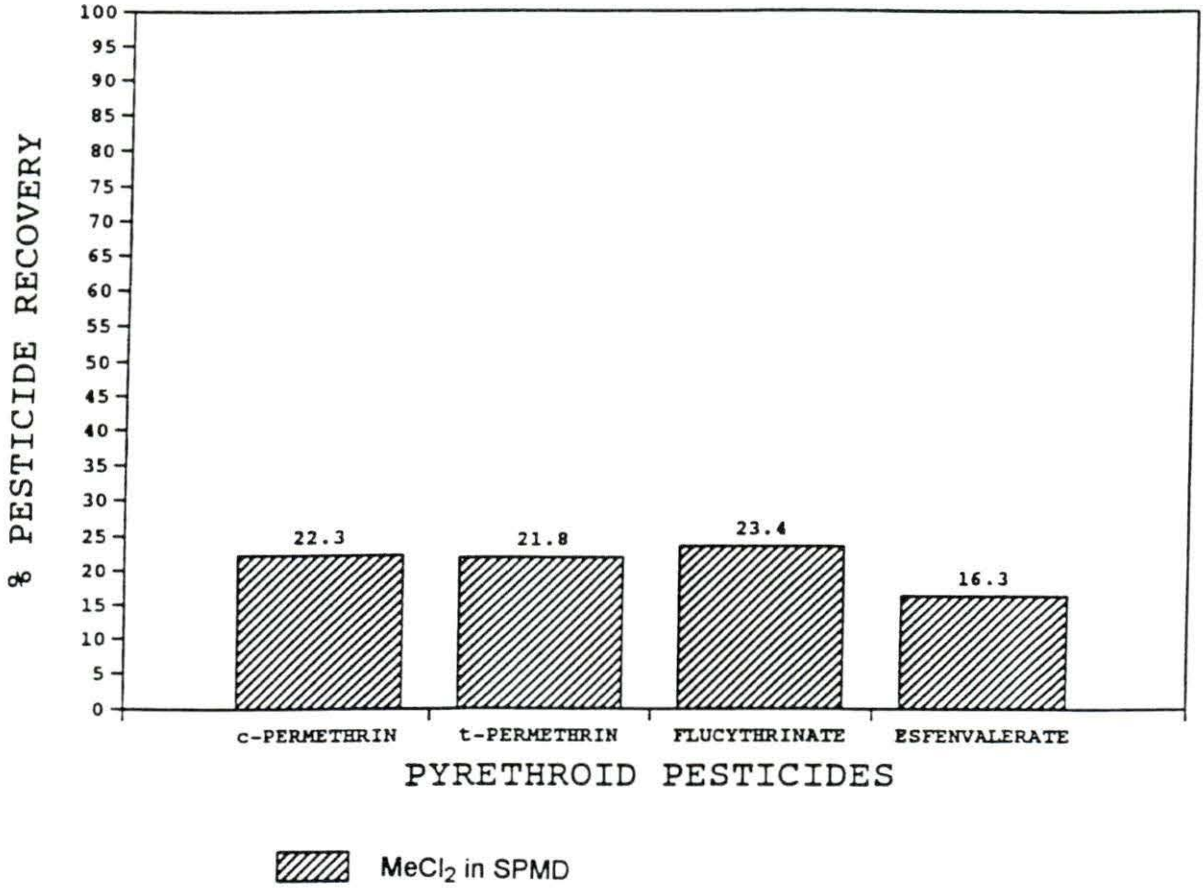

Figure 4. Recovery of pyrethroid pesticides from water using a solvent-containing semipermeable membrane device

Recovery in the $MeCl_2$ within the SPMD for all four pyrethroids is fairly low; in the 20% range. This is contrary to what would be expected for these compounds considering that they have relatively high log Kow values, poor water solubility, and good solubility in $MeCl_2$. It is very likely that a high percentage of these compounds was retained by the polyethylene matrix of the SPMD. Tests performed by Huckins et al. (1990) with fenvalerate showed levels of 25% retained in the polyethylene matrix of the SPMD. Their test exposure lasted 21 days as opposed to this test of 24 hours. It may take longer than 24 hours to establish an equilibrium between the polyethylene membrane and the enclosed solvent, resulting in high levels of pesticide being trapped in the membrane layer after only 24 hours exposure. Again, further testing needs to be done to extract the water fraction and polyethlylene membrane device to determine how the unrecovered pyrethroids are distributed.

Test 5. Recovery of Organophosphate Pesticides

This test measured the effectiveness of a $MeCl_2$-filled SPMD in the recovery of organophosphate pesticides from water. Test procedures and parameters are unchanged from the previous tests. Data is listed in Tables 5A and 5B and in Figure 5A and 5B.

Recovery of all the organophosphate pesticides in the $MeCl_2$ of the SPMD was very good except for dimethoate. Poor recovery of dimethoate could be expected based on its very good water solubility (25,000 ppm at 25°C) and its low log Kow of 0.79. Recovery was good for all the organophosphate compounds tested which had log Kow values over 2.0. From the data, it appears that a very low percentage of the organophosphate compounds are retained in the polyethylene membrane matrix. This may be due to the more selective solubility properties exhibited by organophosphates.

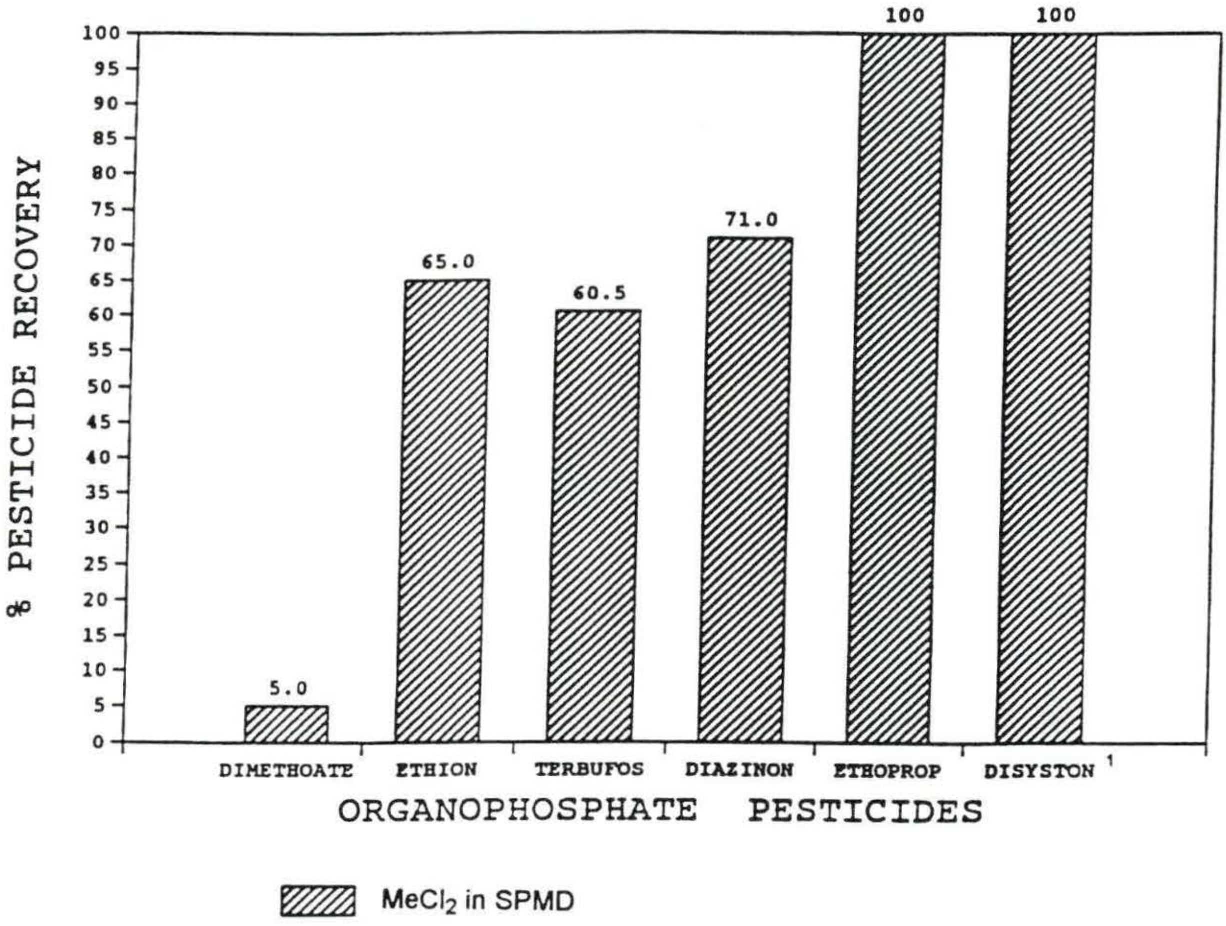

Figure 5. Recovery of organophosphate pesticides from water using a solvent-containing semipermeable membrane device. [1]Common name is disulfoton

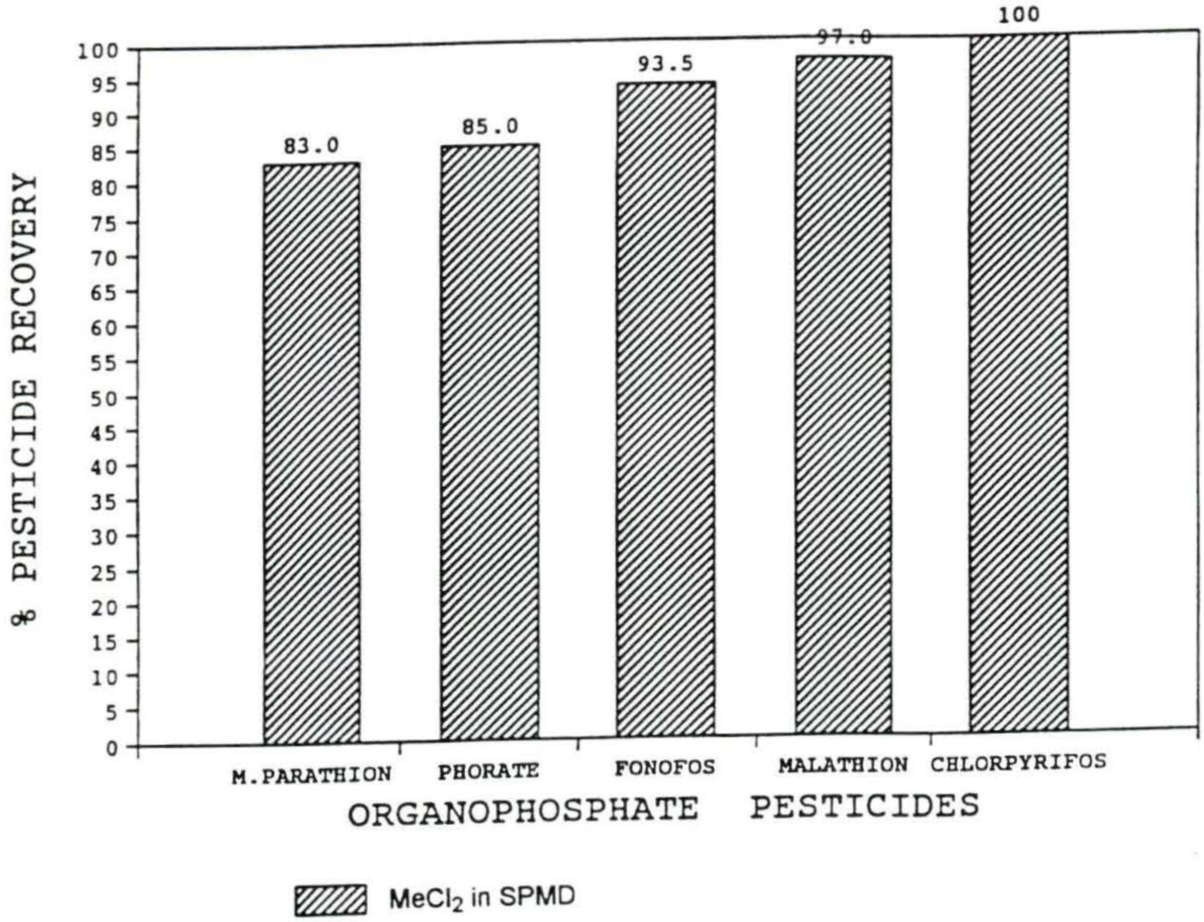

Figure 5. (Continued)

Table 5. Recovery of Organophosphate Pesticides Using a $MeCl_2$-Filled SPMD in a 24-Hour Test

A. Physical Test Data

Container No.	Description	Recovery of $MeCl_2$ in SPMD per 100 ml
1	Blank	76
2	Spike 1A	77
3	Spike 1B	78
4	Spike 2A	78
5	Spike 2B	77
6	Spike 3A	75
7	Spike 3B	76

B. Pesticide Recovery Data

Spike	Pesticide	Amount Spiked (ppb)	Average Percent Recovery in the $MeCl_2$ Fraction
Spikes 1A and 1B	Dimethoate	10.2	5.0
Spikes 1A and 1B	Terbufos	10.2	60.5
Spikes 1A and 1B	Disulfoton	9.2	100+.0
Spikes 1A and 1B	Malathion	9.8	97.0
Spikes 2A and 2B	Ethoprop	10.6	100+.0
Spikes 2A and 2B	Diazinon	9.8	71.0
Spikes 2A and 2B	Chlorpyrifos	10.3	100+.0
Spikes 3A and 3B	Phorate	10.8	85.0
Spikes 3A and 3B	Fonophos	10.0	93.5
Spikes 3A and 3B	Methyl parathion	9.9	83.0
Spikes 3A and 3B	Ethion	10.6	65.0

Test 6. Recovery of Triazine Herbicides

The test measured the recovery of the triazine herbicides atrazine, cyanazine and metribuzin from water. Test procedures and parameters were identical to those set forth in the previous tests.

Overall, the recovery of triazines was not very good. However, the recovery of atrazine (69.5%) was significantly better in this test then in Test 1, where atrazine recovery was only 35.2%. This difference cannot be readily explained. The low recoveries of metribuzin (17.3%) and cyanazine (10.2%) could be expected considering their higher water solubilities and lower log Kow values. Test results are given in Tables 6A and 6B and in Figure 6.

Table 6. Recovery of Triazine Herbicides Using a $MeCl_2$-Filled SPMD in a 24 Hour test

A. Physical Test Data

Container	Description	Recovery of $MeCl_2$ in SPMD per 100 ml
1	Blank	80 ml.
2	Spike 1A	80 ml.
3	Spike 1B	80 ml.
4	Spike 2A	70 ml.
5	Spike 2B	80 ml.
6	Spike 3A	80 ml.
7	Spike 3B	80 ml.

B. Pesticide Recovery Data

Spike	Pesticide	Amount Spiked ppb	Average Percent Recovery in the $MeCl_2$ Fraction
1A and 1B	Cyanazine	10.2 ppb	10.2
2A and 2B	Atrazine	10.7 ppb	69.5
3A and 3B	Metribuzin	10.3 ppb	17.3

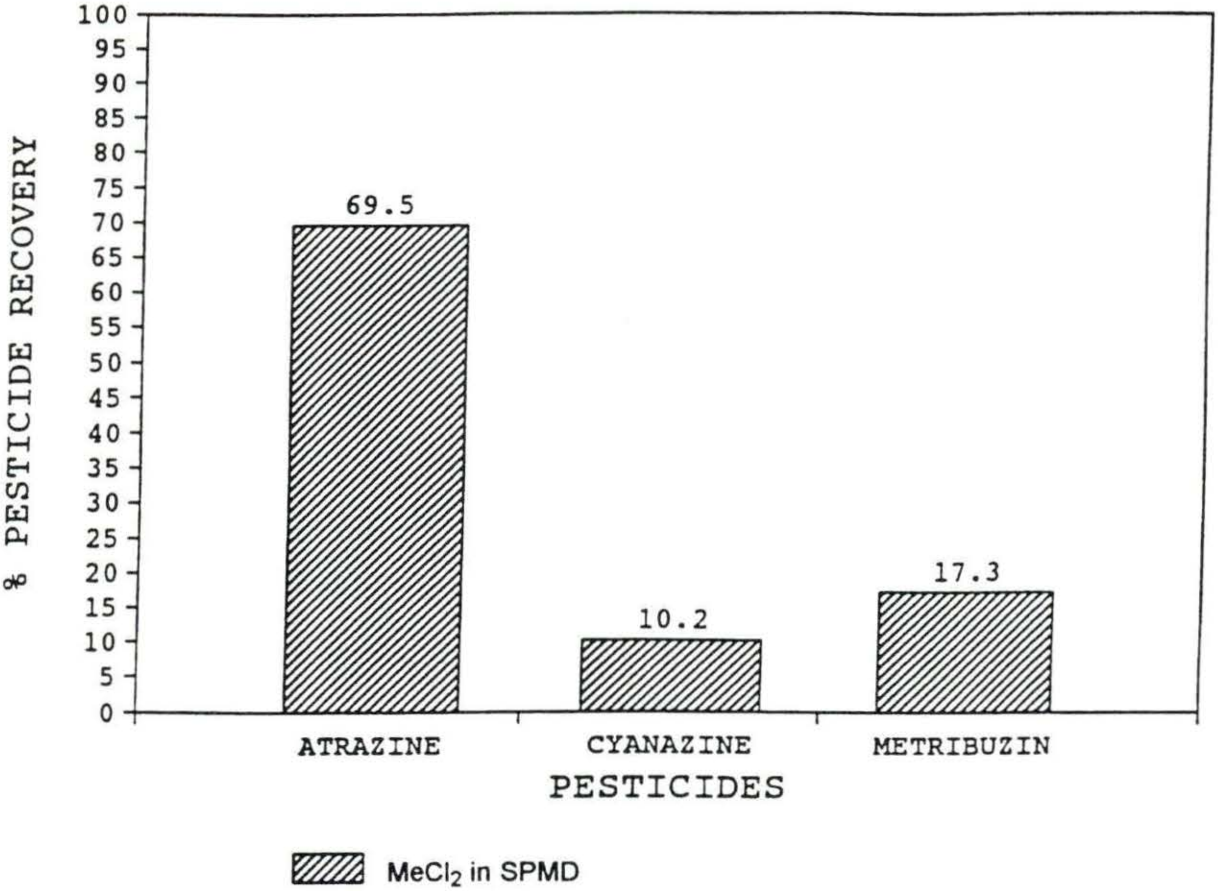

Figure 6. Recovery of triazine pesticides from water using a solvent-containing semipermeable membrane device

CHAPTER 3. SOLVENT COMPARISON STUDIES

In all the previous tests, methylene chloride was used as the receiving solvent contained within the semipermeable membrane bags. The following two tests were designed for the purpose of evaluating the effectiveness of using other solvents within the SPMD to extract pesticides from water.

Test 1. A Study of the Effectiveness of Selected Solvents When Used within a SPMD in Extracting Organophosphate Pesticides from Water

In this test, five different solvents are used in the SPMD to extract organophosphate pesticides from water: methylene chloride, ethyl acetate, hexane, methanol, and acetonitrile. The organophosphate pesticides ethoprop, chlorpyrifos, and diazinon were chosen for this study because the organophosphate pesticides appeared to be less affected by absorption into the polyethylene membrane itself. This would provide a better look at diffusion of the pesticide from the contaminated water medium into the absorbing solvent with less effect from the membrane absorption factor.

Conditions and procedures for the test were the same as in previous tests, using a glass jar containing 1000 ml of water spiked with the three pesticides as the test apparatus. Exposure time for the test was 24 hours. Water temperature was allowed to remain at ambient temperature and was measured at 70°F (21°C) at the start of the test and 78°F (25.5°) at the end of the test.

Test data is given in Table 7. Pesticide recovery data is presented in Table 8 and Figure 7. For all tests, ethoprop was spiked into water at a level of 10.6 ppb. Diazinon was spiked at 9.8 ppb and chlorpyrifos was spiked at 10.3 ppb.

Table 7. Physical Test Data for Solvent Comparison Study

Test Container	**Description**	**Recovery of Solvent in SPMD per 100 ml**
1	Blank ($MeCl_2$)	76 ml
2	Methylene chloride spike	79 ml
3	Methanol spike	95 ml
4	Hexane spike	85 ml
5	Acetonitrile spike	94 ml
6	Ethyl acetate spike	86 ml

Table 8. Spike Recovery Data for Solvent Comparison Test

Extraction Solvent	**Dielectric Constant at Room Temperature**	**% Pesticide Recovery Ethoprop**	**% Pesticide Recovery Diazinon**	**% Pesticide Recovery Chlorpyrifos**
Methylene Chloride	9.08	86.3	80.8	62.3
Methanol	32.63	3.4	20.8	44.6
Hexane	1.89	53.8	67.3	66.0
Acetonitrile	38.80	4.9	37.3	61.6
Ethyl Acetate	6.20	21.2	62.2	82.8

The solvent which resulted in the highest recovery of the three pesticides was $MeCl_2$, followed by hexane and ethyl acetate. Poorer recoveries were obtained using acetonitrile and methanol. The solvents producing the best recoveries exhibit low to moderate polarity. The high polarity solvents: methanol (dielectric constant = 32.63 at room temp.) and acetonitrile (dielectric constant = 38.80 at room temp.) achieved poor recoveries. These results are consistent with the moderate log Kow values and the low water solubility of the three compounds. The compounds would be more likely to diffuse from water to a nonpolar solvent than into a polar solvent.

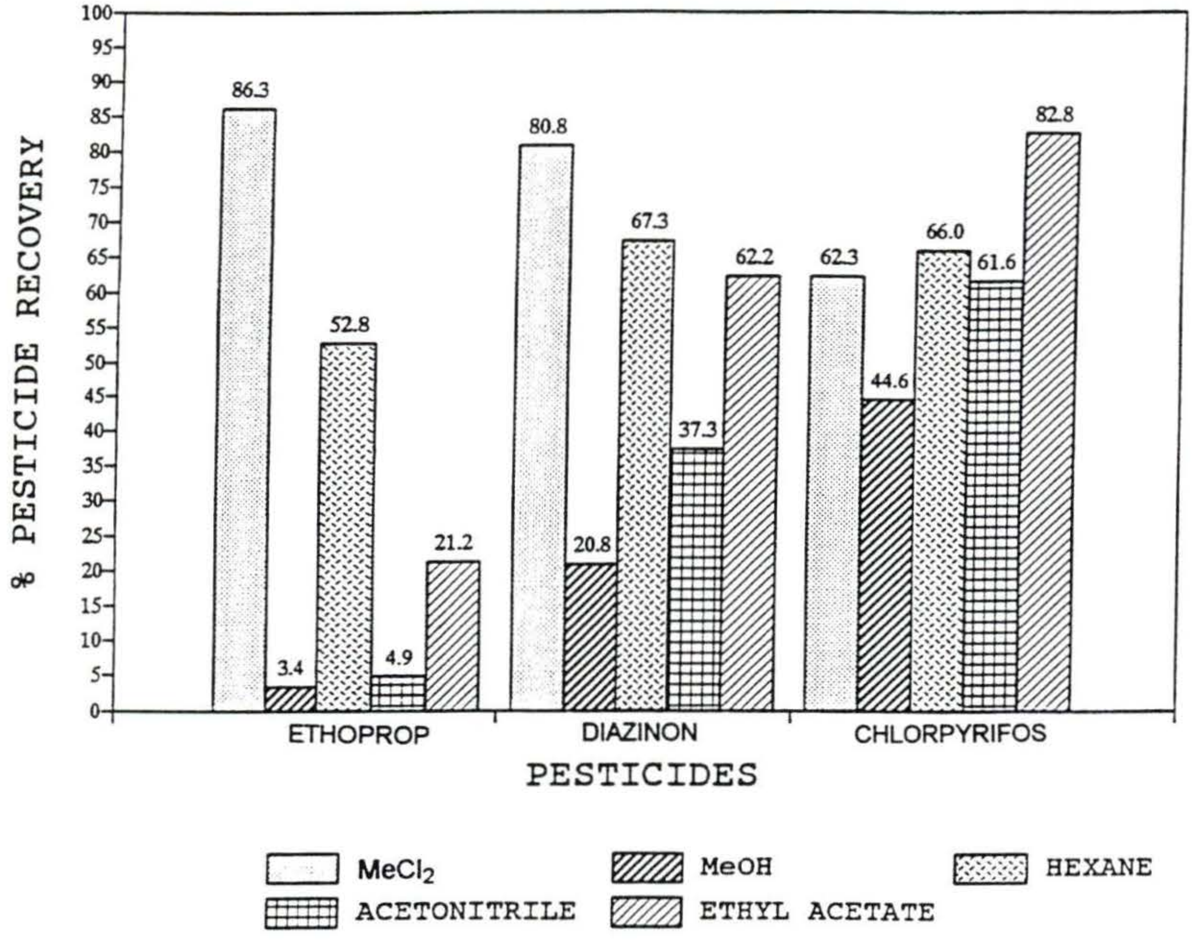

Figure 7. Comparison of the effectiveness of various solvents in the recovery of organophosphate pesticides from water using a solvent-containing semipermeable membrane device

Test 2. Comparison of the Effectiveness of Methylene Chloride and Ethyl Acetate When Used in a SPMD to Extract Pesticides from Water

In this test $MeCl_2$ and ethyl acetate were used in the SPMD to compare their effectiveness in extracting pesticides belonging to various families from water. Dieldrin, an organochlorine, atrazine, a triazine, carbofuran, a carbamate, chlorpyrifos, a chlorinated organophosphate, and trifluralin, a dinitroaniline were spiked into water in a test container. A SPMD containing $MeCl_2$ and another containing ethyl acetate were placed in separate test containers for an exposure period of 24 hours. After 24 hours, the solvents were removed from the bags and analyzed for pesticide recovery. Test procedures and parameters were identical to conditions used in the previous tests.

Summary of the test data and pesticide recoveries are given in Tables 9 and 10 and in Figure 8. The results indicate that $MeCl_2$ and ethyl acetate were comparable in their ability to extract trifluralin, chlorpyrifos, and dieldrin from water. Where $MeCl_2$ was fair in recovering the triazine, atrazine, and the carbamate, carbofuran from water, ethyl acetate was completely ineffective in recovering these compounds.

Table 9. Physical Test Data For Comparison of $MeCl_2$ and Ethyl Acetate

Container	Description	Recovery of Solvent in SPMD per 100 ml
1	$MeCl_2$ Spike A	82
2	$MeCl_2$ Spike B	82
3	Ethyl Acetate Spike A	86
4	Ethyl Acetate Spike B	85

Table 10. Recovery Results -- $MeCl_2$ vs. Ethyl Acetate(E.A.)

Pesticide	**Spike Level (ppb)**	**Average Pesticide Recovery Using $MeCl_2$ (%)**	**Average Pesticide Recovery Using E.A. (%)**
Trifluralin	1.0 ppb	62.5	70.0
Atrazine	10.7 ppb	47.0	0.0
Chlopyrifos	10.3 ppb	70.0	72.0
Dieldrin	10.5 ppb	70.0	76.5
Carbofuran	10.0 ppb	37.5	0.0

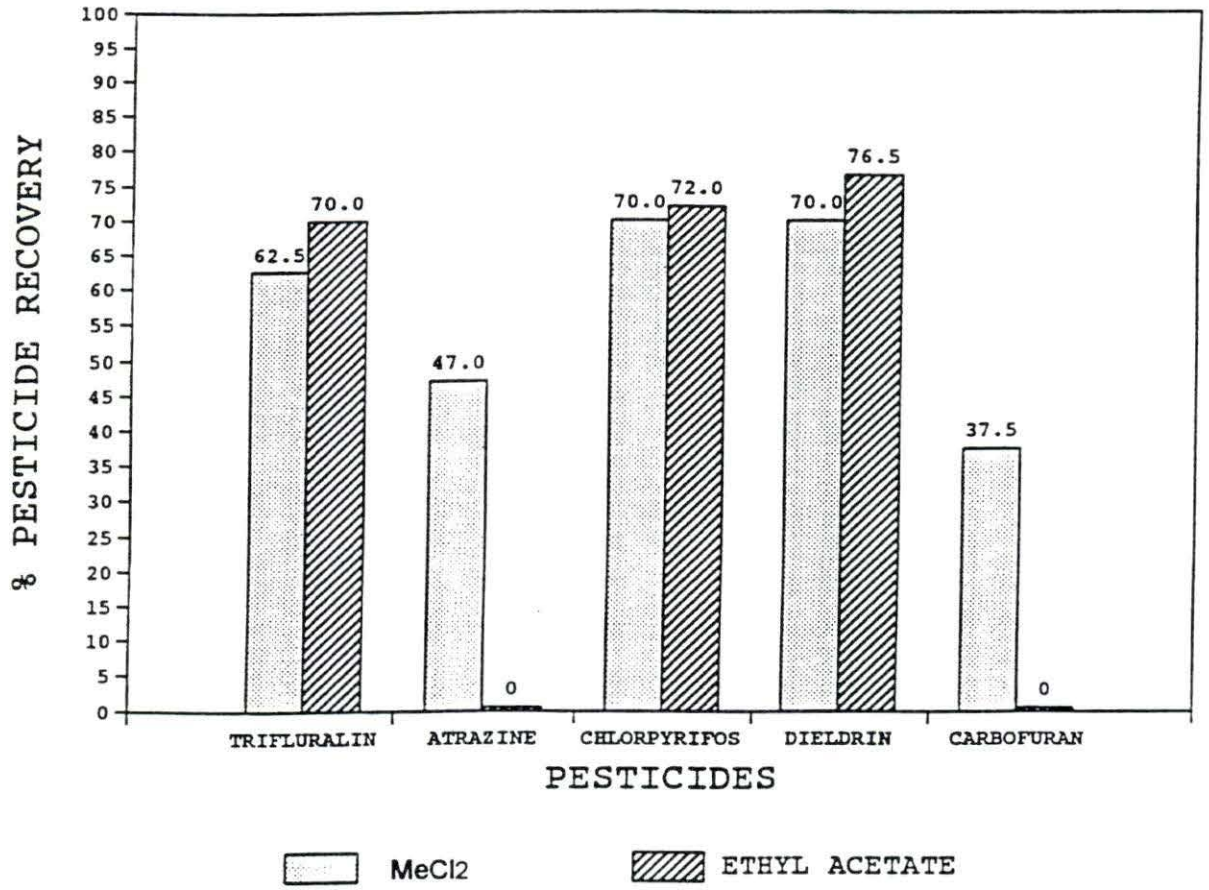

Figure 8. Comparison of methylene chloride and ethyl acetate in the recovery of pesticides from water using a solvent-containing semipermeable

CHAPTER 4. TIME STUDY - ABSORPTION OF PESTICIDES OVER TIME USING A SPMD CONTAINING ETHYL ACETATE

The purpose of this test was to measure how rapidly various pesticides could be absorbed from water by a SPMD containing ethyl acetate. The ethyl acetate in the SPMD was monitored for pesticide content at various time intervals from the time of initial exposure to a time of 24 hours to determine the percent absorption over time.

Table 11. Time Intervals and Ethyl Acetate Recovery

Container No.	**Time Interval (A and B Represent Duplicates)**	**Ethyl Acetate Recovered from the SPMD per 100 ml**
1	5 minute (A)	97
2	5 minute (B)	97
3	10 minute (A)	97
4	10 minutes (B)	98
5	15 minutes (A)	98
6	15 minutes (B)	98
7	20 minutes (A)	98
8	20 minutes (B)	98
9	30 minutes (A)	98
10	30 minutes (B)	98
11	1 hours (A)	97
12	1 hour (B)	97
13	2 hours (A)	97
14	2 hours (B)	97
15	4 hours (A)	97
16	4 hours (B)	97
17	8 hours (A)	96
18	8 hours (B)	95
19	24 hours (A)	88
20	24 hours (B)	90

Amber glass jars containing 1000 ml of water were used as test containers. All containers were spiked with 10 ppb of atrazine, metolachlor, chlorpyrifos, carbofuran and dieldrin. Polyethylene membrane devices (SPMDs) containing 100 ml of ethyl acetate were placed in these containers. The SPMD's were then removed after a specific time interval and the ethyl acetate was analyzed for pesticide content. Water temperature was maintained at room temperature (21.1°C) for all tests. Time intervals and ethyl acetate recovery are listed in Table 11.

Test results showed no recovery of atrazine, metolachlor, or carbofuran even after 24 hours exposure time, indicating that ethyl acetate was a poor choice of solvents for these three compounds. Rate of recovery of chlorpyrifos and dieldrin over time are shown in Table 12 and Figure 9.

Table 12. Chlorpyrifos and Dieldrin Recovery Over Time

Time of Exposure	**Average % Dieldrin Recovery**	**Average % Chlorpyrifos Recovery**
24 hours	(Spike level = 10.5 ppb) 30.5	(Spike Level = 10.3 ppb) 46.0
8 hours	14.4	21.0
2 hours	2.1	6.2
1 hour	1.2	3.5
30 minutes	0.0	1.8
5,10, 15 and 20 minutes	0.0	0.0

Both compounds show very little recovery over the first two hours of exposure. Pesticide absorption gradually increases up to the 24 hour exposure time, but it did not reach the 70% levels that were achieved in the ethyl acetate vs. $MeCl_2$ comparison test for the two compounds. It appears that equilibrium had not been reached even after 24 hours. Assuming that there is some absorption of the compounds by the polyethylene membrane device itself, there is most likely a lag

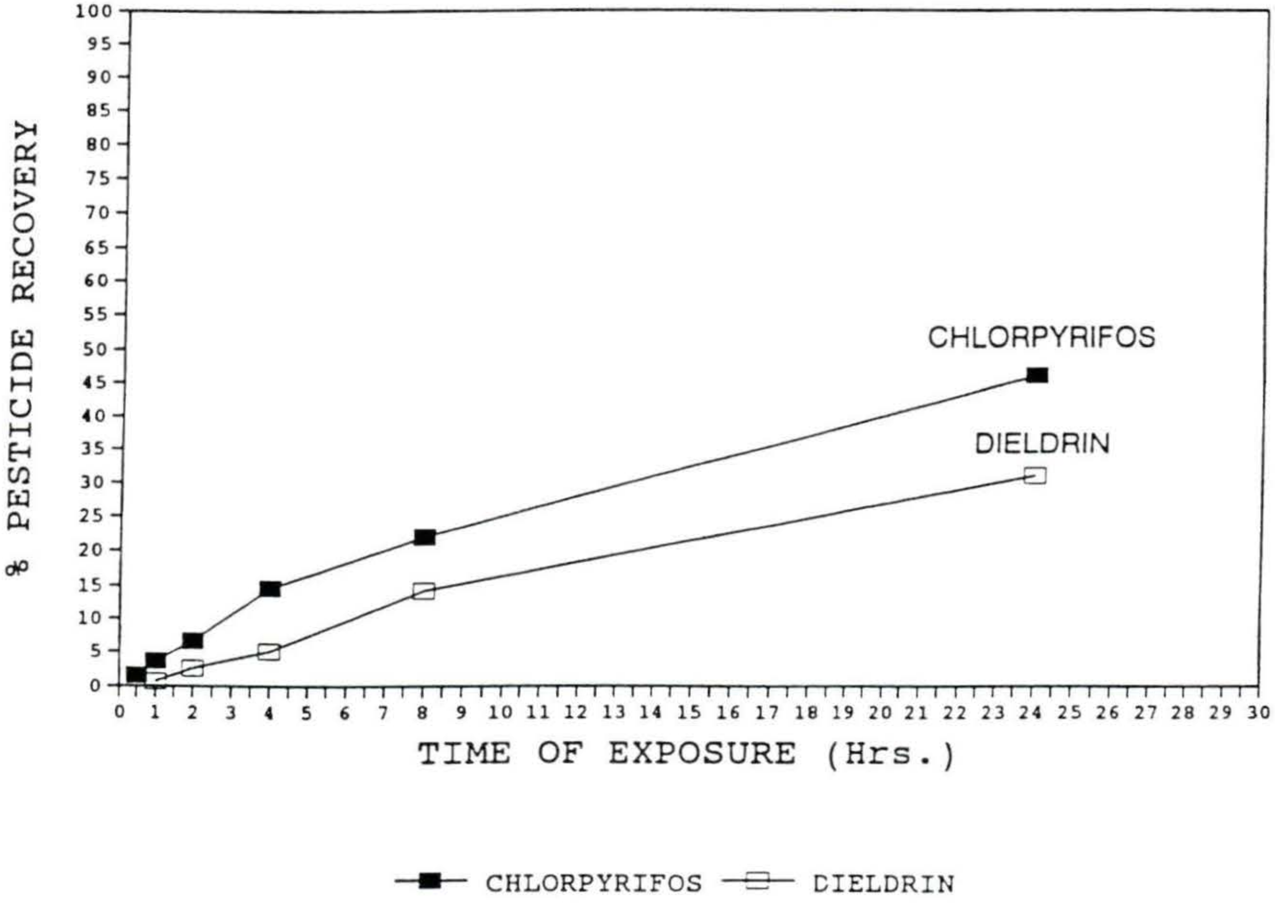

Figure 9. Time Study: Recovery of dieldrin and chlorpyrifos from water using a ethyl acetate-containing SPMD over time

time when the pesticide is being absorbed by the membrane and before it begins diffusion into the ethyl acetate solvent within the SPMD. Additional time studies extended beyond 24 hours would need to be performed to determine at what time equilibrium is reached and the percent absorption level for each compound at equilibrium. Absorption rates for each compound would be expected to vary depending on the solvent used in the SPMD.

CHAPTER 5. EFFECT OF WATER TEMPERATURE ON PESTICIDE ABSORPTION BY A SPMD

The purpose of this study was to observe the effects of water temperature on the absorption of pesticides by a SPMD containing $MeCl_2$. Recovery of five different pesticides, all from different pesticide families, was determined at three temperature levels: 3.3°C, 20°C, and 27°C. (Note: A temperature study at 38° C was attempted, but failed due to a complete loss of $MeCl_2$ in the membrane bag over 24 hours) . The pesticides involved in the study were trifluralin, atrazine, dieldrin, chlorpyrifos, and carbofuran. The time of exposure was 24 hours. Parameters and test procedures remained unchanged from earlier tests, except that the designated water temperatures were maintained throughout the test. Test data for the temperature study is given in Table 13.

Table 13. Temperature study test data

Container No.	**Temperature of Test**	**Recovery of $MeCl_2$ in the SPMD per 100 ml**
1	Blank - 20°C (68°F)	80 ml
2	3.3°C-A (38°F)	80 ml
3	3.3°C-B	82 ml
4	20°C-A (68°F)	80 ml
5	20°C-B	80 ml
6	27°C-A (81°FC)	80 ml
7	27°C-B	79 ml
8	38°C-A (100°F)	0
9	38°C-B	0

The test results for the temperature study are given in Table 14 and Figure 10. Analysis of the results would indicate that the compounds trifluralin, chlorpyrifos, and dieldrin, which have the highest log Kow values and the lowest water solubility were absorbed better at the lower water temperature. The opposite

Table 14. Summary of Temperature Study. The recovery of trifluralin, atrazine, chlorpyrifos, dieldrin, and carbofuran from water at various temperatures using a semipermeable membrane device filled with methylene chloride

Pesticide	Spike Level (ppb)	% Spike Recovery at 3.3°C	% of Spike Recovery at 20°C	% Spike Recovery at 27°C
Trifluralin	1.04 ppb	79.0	72.5	50.0
Atrazine	10.7 ppb	3.0	52.0	60.5
Chlorpyrifos	10.3 ppb	84.5	76.5	60.5
Dieldrin	10.5 ppb	65.5	49.5	28.0
Carbofuran	10.0 ppb	0.0	35.0	42.5

a. Time of exposure = 24 hours

appears to be true for the compounds atrazine and carbofuran. They have higher water solubility and lower log Kow, and appear to be absorbed more by the $MeCl_2$ SPMD at higher water temperatures.

It could be theorized that lower water temperature decreased the water solubility of dieldrin, chlorpyrifos, and trifluralin even more and created a shift in equilibrium favoring $MeCl_2$ solubility. This could facilitate a higher diffusion of these compounds into $MeCl_2$ at a lower water temperature. Conversely higher temperatures made these three compounds more water soluble and decreased passive diffusion across the membrane. In the case of atrazine and carbofuran, increased water temperature and the accompanying increase in $MeCl_2$ temperature may have shifted the equilibrium in such a way as to increase $MeCl_2$ solubility for these compounds. Recovery of the triazine, atrazine and the carbamate, carbofuran by the $MeCl_2$ containing SPMD was much greater at 27°CF than at 3.3° C. Also, temperature changes could change the permeability of the membrane matrix, which would then affect diffusion rates of the different compounds. It is very

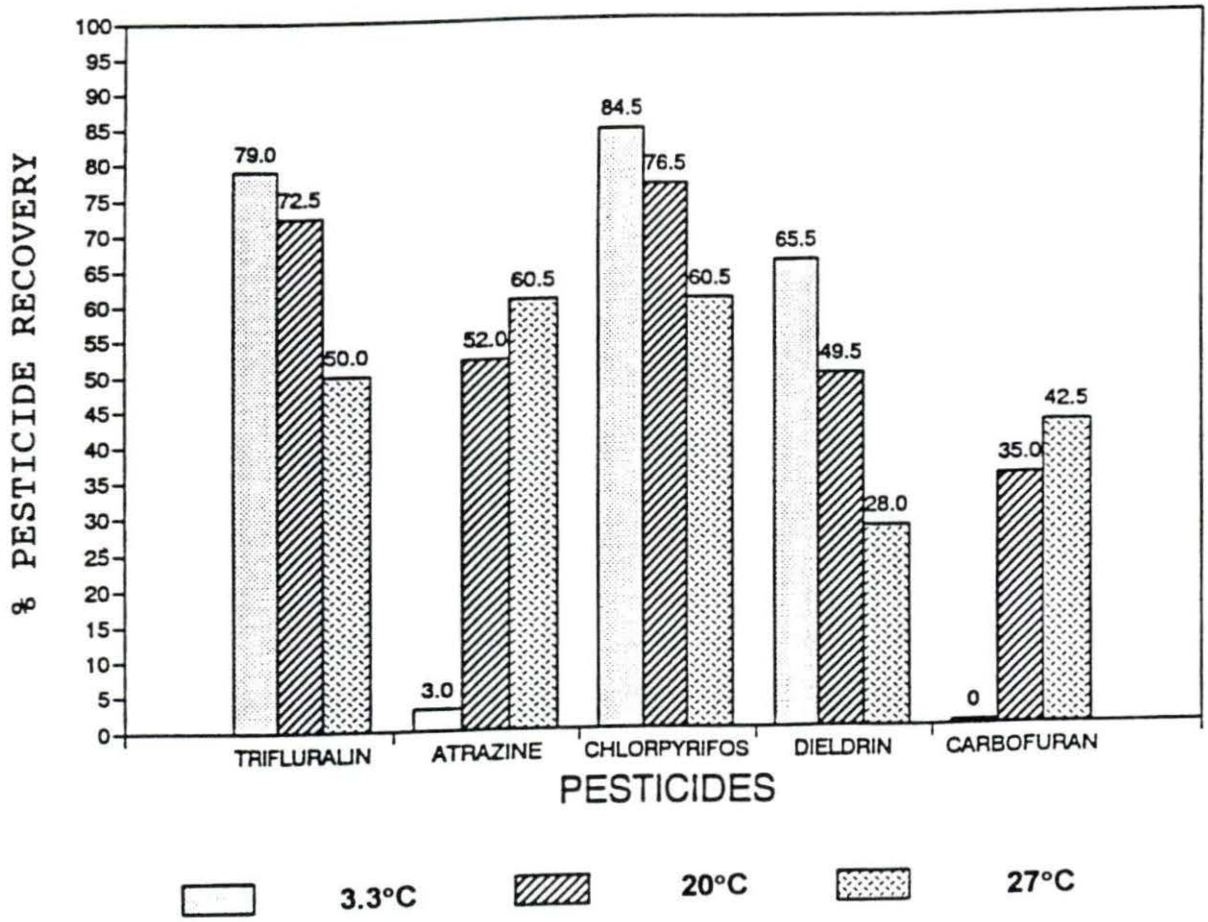

Figure 10. Temperature Study: Recovery of pesticides from water at various temperatures using a semipermeable device filled with $MeCl_2$

likely that water solubility, solvent solubility, and membrane permeability are all factors that change along with a change in water temperature; and that these changes affect the degree of diffusion of any particular pesticide into the solvent within the SPMD.

CHAPTER 6. ABSORPTION OF PESTICIDES FROM WATER USING A SPMD CONTAINING ONE GRAM OF TRIOLEIN

The purpose of this test was to evaluate a SPMD containing a lipid such as triolein rather than a solvent-containing SPMD as a means of monitoring pesticide contamination in water.

Lay-flat polyethylene tubing was used as the SPMD. This device was similar to the one developed by Huckins et al. (1980). It consisted of a lay-flat polyethylene tube which was 18 inches (45.72 cm) long and one inch (2.54 cm) wide. The membrane thickness was 80 um (micron).

The SPMD was prepared by cutting a 22-inch strip of tubing. One end of the tubing was sealed using a plastic bag sealer (Deni Freshlock Vacuum Sealer) and the seal was then checked for leaks. One gram of triolein was weighed into each tube. The triolein was then pressed into the tube producing a thin layer of triolein throughout the tube. All the air was pressed out of the tube. The top of the tube was then sealed, resulting in a 22-inch lay-flat polyethylene SPMD containing a thin layer of triolein. At each end of the tubing, two inches of tubing was wrapped end over end several times and clipped with a paper clip. This was done to help assure that the tube would not leak at the sealed ends. The triolein was pressed out of the 2-inch end segments toward the center of the tubing before the end segments were folded. Eighteen inches of tubing was thus exposed. Total surface area of tubing exposed in the test was 36 square inches (232 sq cm.). Each SPMD was weighed before and after the test exposure to determine if there was any loss of triolein.

The polyethylene tube was then placed into a test apparatus which consisted of a metal cage 12.5 cm wide x 10 cm deep x 10 cm high. The cage acted to protect the SPMD during exposure and also acted as an anchor to hold the SPMD in place.

At the same time, it allowed the free flow of water around the SPMD surface. The cage was a box structure made of small metal bars spaced about one cm apart. The bottom of the cage was layered with metal balls contained within a sealed plastic bag. This acted as a weight to hold the cage down in the water. The 18-inch-long SPMD was hung in the top half of the cage by weaving it from one end of the cage to the other. Metal clips were used to secure the SPMD to the cage at each end of the tubing. The cage top was then covered with a metal screen. Nylon cord was used to secure the screen top to the cage.

For the test, 2000 ml of tap water was added to two metal containers which were large enough to hold the SPMD test apparatus. The water in one container was spiked with the pesticides trifluralin, atrazine, chlorpyrifos, dieldrin, and carbofuran at a level of 10 ppb (1.0 ppb for trifluralin). The second container was left untreated and served as a control. A test apparatus was placed in each container so that it was completely submerged. The test apparatus was left in place for an exposure period of one week at ambient temperature. After one week the SPMD was removed and the triolein was analyzed for the presence of pesticides. At this time a triolein spike was set up, where one gram of triolein was spiked directly with the pesticides to test for recovery of pesticide through the extraction procedure.

The pesticides were extracted from the triolein using the following procedure:

1. The SMPD (tubing) was removed from the cage.
2. The SPMD was washed with distilled H_2O and gently dried with a paper towel.
3. The SPMD was weighed to determine if any triolein loss had occurred, and the weight was recorded.

4. A small piece was cut off at one end of the tubing to open the SPMD.
5. The triolein was squeezed out of the SMPD into a 125-ml beaker.
6. The SPMD was rinsed four times with 4 - 5 ml of hexane to remove all triolein (Total volume of hexane = 25 ml.)
7. The hexane containing the triolein was transferred to a 500-ml separatory funnel.
8. Fifty ml of acetonitrile was added to the funnel, and it was shaken for thirty seconds.
9. The 125-ml beaker was rinsed with 25 ml of hexane, and the hexane was added to the separatory funnel.
10. The separatory funnel was shaken for 30 seconds, and the layers were then allowed to separate.
11. The bottom (acetronitrile) layer was drained into a 400-ml beaker and saved.
12. The hexane was extracted once more with 25 ml of acetonitrile.
13. The combined acetonitrile extract was saved, and the hexane layer discarded.
14. The acetonitrile was poured back into the separatory funnel and washed with another 25 ml of hexane.
15. The bottom acetonitrile layer was saved and the hexane discarded.
16. Forty ml of distilled water was added to the acetonitrile.
17. The acetonitrile/water mixture was poured into a clean, 500 ml separtory funnel containing 100 ml of 2% NaCl solution.
18. One hundred ml of $MeCl_2$ was added to the separatory funnel and the funnel was shaken for one minute to extract the pesticides.

19. The bottom ($MeCl_2$) layer was drained through Whatman No. 1 filter paper containing 3 grams of anhydrous sodium sulfate into a 250-ml Erlenmeyer flask.
20. The acetonitrile was extracted once more with 25 ml of $MeCl_2$, and the extracts were combined.
21. The $MeCl_2$ was concentrated on a hot plate at low heat with nitrogen to 2-3ml.
22. The sample was then transferred with $MeCl_2$ to a 15 ml-volumetric tube.
23. The sample was concentrated with N_2 to near dryness.
24 The sample was then brought up to a 5-ml volume with hexane for analysis.
25. The sample was analyzed for trifluralin, chlorpyrifos, atrazine and dieldrin using a gas chromatograph, and analyzed for carbofuran using thin layer chomatography analysis.

The results of the analysis are given in Tables 15 and 16 and in Figure 11. Loss of triolein from the tubing over the one-week exposure period was fairly small. The blank showed a 7% loss, and the water spike had a 2% loss. The SPMD containing triolein was ineffective in recovering the triazine, atrazine and the carbamate, carbofuran. Recoveries were fair for trifluralin and dieldrin, and good for chlorpyrifos. It would be expected from their low log Kow values that atrazine and carbofuran would be the most difficult to recover. Dieldrin recovery would be expected to be higher than the 37% level attained considering its high log Kow and

Table 15. Test Data for the Absorption of Pesticides from Water Using a SPMD Containing Triolein

Time for start of test - 9:20 AM (Wednesday, 7/27/94)		
Time for end of test - 9:00 AM (Wednesday, 8/3/94)		
Total time fo test - Seven (7) days (168 hours)		
H_2O Temperature at start of test - 70° F(21.1°C)		
H_2O Temperature at end of test - 75° F (23.9°C)		
	Blank	**Spike**
SPMD weight before test	3.38g	3.46g
SPMD weight after test	3.31g	3.44g
TOTAL WEIGHT LOSS	.07g	.02g

Table 16. Pesticide Recovery from a SPMD Containing One Gram of Triolein

Pesticide	**Amount Spiked (ppb)**	**SPMD with Triolein - % Recovery**	**Direct Triolein Spike - % Recovery**
Trifluralin	1.0 ppb	24.4	88.6
Atrazine	10.7 ppb	0.0	82.5
Chlorpyrifos	10.3 ppb	70.9	100+.0
Dieldrin	10.5 ppb	37.0	67.2
Carbofuran	10.0 ppb	0.0	75.0

poor water solubility. It is quite likely that a large portion of the dieldrin was absorbed by the nonpolar membrane matrix. Also, results of pesticide recovery from the triolein, which was spiked directly, showed that dieldrin had the poorest carry-through in the extraction and clean-up procedure. The other pesticides were carried through the extraction procedure fairly well.

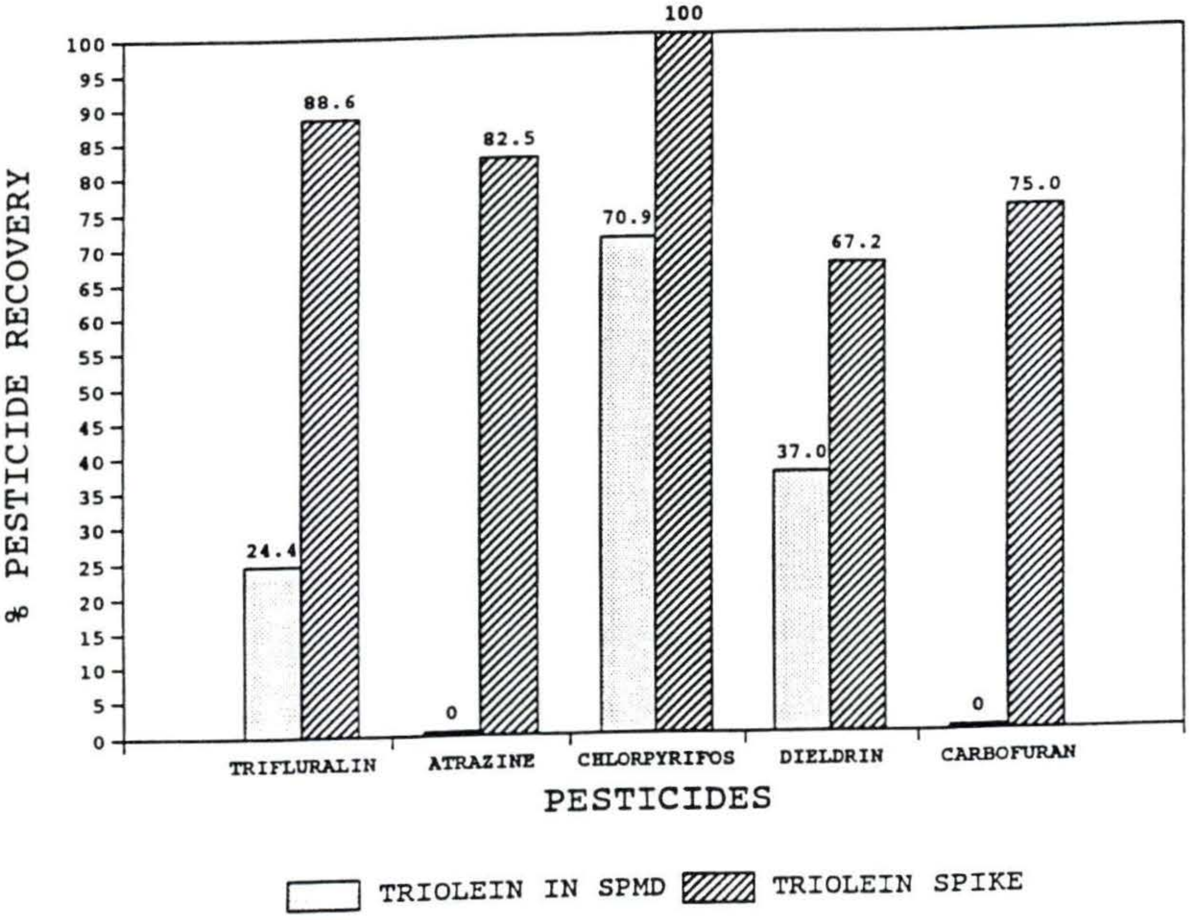

Figure 11. Recovery of pesticides from water using an 18 inch SPMD containing 1.0 Gram of triolein. Exposure time = one week

Results of the test indicate that the SPMD containing triolein could be effective for monitoring water for nonpolar pesticides with higher log Kow values and low water solubility, but would be ineffective in absorbing many of the more water soluble triazine herbicides and carbamate insecticides.

CHAPTER 7. FIELD STUDIES

Field Tests were performed using SPMD's to determine their effectiveness In monitoring pesticide contamination in actual lake and stream settings. These studies were performed at Don Williams Lake, a 180-acre artificial lake located five miles north of Ogden in Boone County, Iowa. The lake has 37 miles of shoreline and a maximum depth of 48 feet. The watershed for the lake drains agricultural land used primarily for the growing of corn and soybeans and as pasture land.

Four test sites were selected around the lake. (See Figure 12 for Map.)

Site A - Located in the major stream entering the lake under the bridge at the north end of the lake on Boone County Road P-70. The test apparatus was placed on the stream bottom in the middle of the stream in about 2 feet of water.

Site B - Located in a small cove at the N.E. corner of the lake. The apparatus was suspended 2 feet below the surface in 6 feet of water.

Site C - Located at the boat docks west of the bait house and boat ramp. The apparatus was suspended 2 feet below the surface in about 12 feet of water.

Site D - Located in the stream below the spillway and dam about 30 yards down stream from the spillway pond. The apparatus was placed on the stream bottom in about 2 feet of water.

The test apparatus consisted of a SPMD placed in a metal cage device. The test apparatus was similar to the one described in Chapter 6 except that a 7-inch x 8-inch polyethylene membrane bag, having a membrane thickness of 44.5 um was used. The bag was identical to the SPMD bag used in the lab tests. The bag was filled with 100 ml of methylene chloride and sealed at the top. The top of the

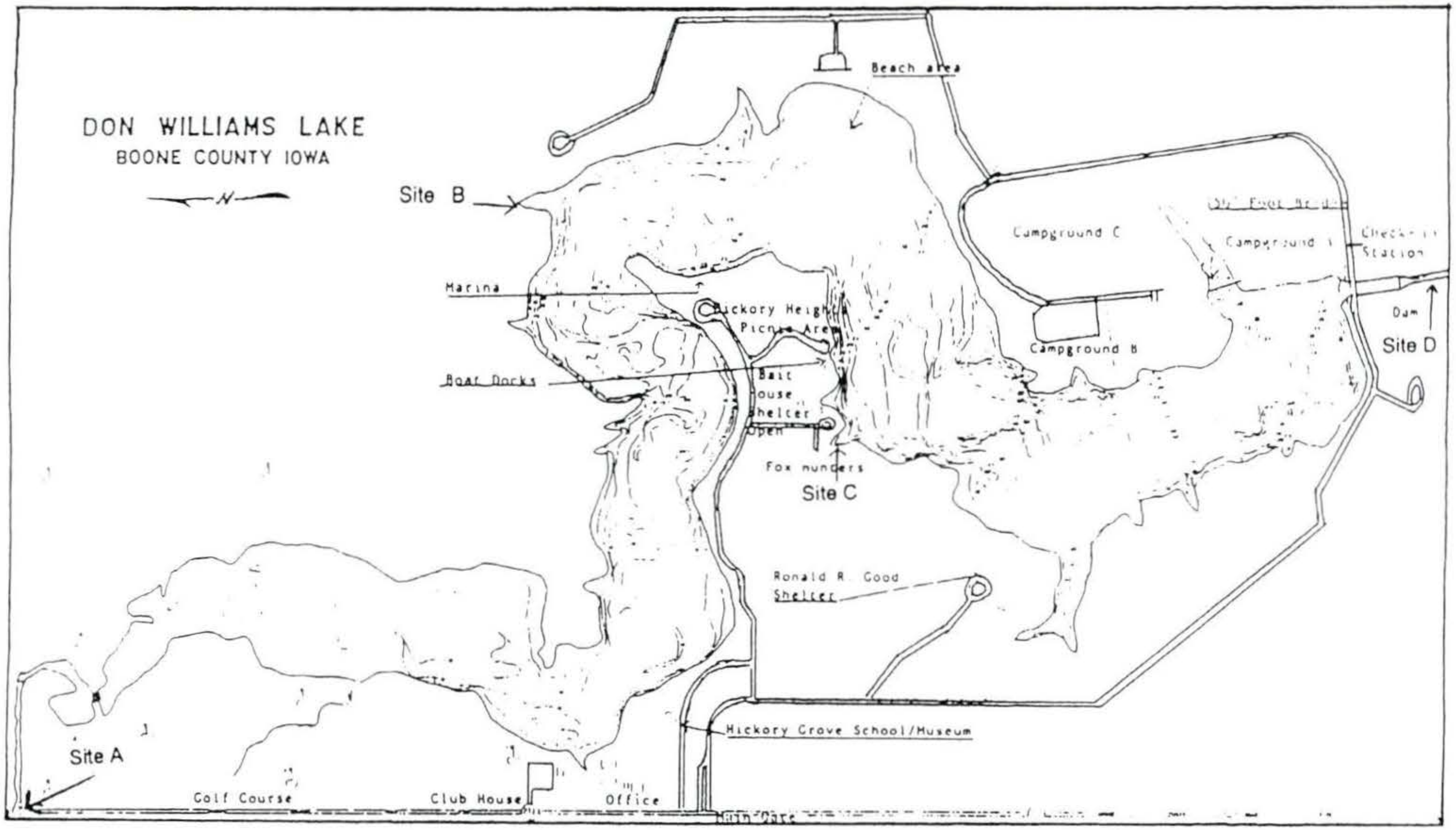

Figure 12. Map of Don Williams Lake Showing Field Testing Sites
(Anthony D., 1974)

bag was also folded over several times and clamped with metal clamps to further protect against leakage. All test devices were secured in place by anchoring them to logs or pilings, and all were tagged for identification. Test devices were placed in the water for a period of 24 hours. Table 17 gives the field study data.

Table 17. Field Study Data For Water Testing at Don Williams Lake Using A SPMD containing $MeCl_2$

	Site A	Site B	Site C	Site D
Water Temp. at Start of Test	64°F (17.8°C)	80°F (26.7°C)	80°F(26.7°C)	79°F(26.1°C)
Time - Start of Test (6-21-94)	10:20 A.M.	11:30 A.M.	10.40 A.M.	11:00 A.M.
Time - End of Test (6-22-94)	10:19 A.M.	11:30 A.M.	10:38 A.M.	10:58 A.M.
Total Exposure Time	24 hr	24 hr	24 hr	24 hr
Solvent Used	$MeCl_2$	$MeCl_2$	$MeCl_2$	$MeCl_2$
Volume of Solvent	100 ml	100 ml	100 ml	100 ml
Solvent Recovery per 100 mls. used	12 ml	O ml	O ml	O ml

At the same time that test devices were placed in the lake, two 1000-ml samples of water were taken from each test site for water analysis. A 1000-ml sample from each site was analyzed for 50 different commonly used pesticides including 13 organochlorines, 12 organophosphates, 5 pyrethroids, 6 carbamates, 5 phenoxy acid herbicides, and nine miscellaneous pesticides. The water fraction was extracted using accepted pesticide extraction methods for water with $MeCl_2$ as the extraction solvent (Wershaw et al., 1987). Water analysis found only two

Table 18. Pesticides Found at Don Williams Lake Using Standard Water Analysis

Site	Metolachlor (ppb)	Atrazine(ppb)
A	0.36	0.67
B	0.13	0.30
C	0.10	0.30
D	0.11	0.28

pesticides, and these were detected at all four sites; metolachlor and atrazine. The levels found at each site are given in Table 18.

Water analysis using the SPMDs filled with 100 ml of $MeCl_2$ proved to be ineffective due to the large loss of solvent from the membrane device over the 24-hour period. All the $MeCl_2$ had diffused from the bags at Sites B, C, and D. At Site A, only 12 ml was retained in the polyethylene bag. Extensive laboratory testing in which the bags were deployed in one liter of water consistently produced solvent losses of only about 20% in a 24-hour test period. Exposure to the much larger volumes of water in the field study appeared to result in a much greater diffusion rate of $MeCl_2$ from the membrane device over the 24-hour period. In lab exposures where water volume is limited to 1000 ml, the water would be more likely to become saturated with $MeCl_2$ and an equilibrium point reached at which time diffusion of $MeCl_2$ from the membrane is slowed. At site A where 12 ml of $MeCl_2$ was retained, the water temperature was lower than at the other three sites, and this probably had an effect in reducing $MeCl_2$ loss from diffusion. Analysis of the 12 ml of $MeCl_2$ retained in the SPMD at Site A detected no atrazine, but found a total of 8.6 ng of metolachlor in the solvent or a concentration of 0.72 ppb in the $MeCl_2$.

Due to the significant loss of solvent from the SPMD, a second field test was performed using a SPMD containing 1 gram of triolein. A test apparatus using an 18-inch polyethylene tubing was constructed as described in Chapter Seven.

A device was employed at each of the four test sites around the lake for a period of 7 days. After 7 days the devices were removed, and the triolein was extracted and analyzed for pesticide following the procedure described in Chapter 6. Loss of triolein over the seven-day period was minimal (See Table 19 for Test Data).

Table 19. Field Study Data for Water Testing at Don Williams Lake Using a Triolein -filled SPMD

Parameter	**Site A**	**Site B**	**Site C**	**Site D**
Water Temp. at Start of Test	72°F (22.2°C)	81°F (27.2°C)	81°F (27.2°C)	80°F (26.7°C)
Water Temp. at End of Test	64°F (17.8°C)	73°F (22.8°C)	73°F (22.8°C)	73°F (22.8°)
Date - Start of Test	7-7-94	7-7-94	7-7-94	7-7-94
Date - End of Test	7-14--94	7-14-94	7-14-94	7-14-94
Total Exposure Time	7 days	7 days	7 days	7 days
Length of SPMD	18 in.	18 in.	18 in.	18 in.
Grams of Triolein Used	1.0g	1.0g	1.0g	1.0g
Wt. of SPMD Start of Test	3.46g	3.40g	3.42g	3.36g
Wt. of SPMD	3.35g	3.41g	3.48g	3.47G
SPMD wt. change	- 0.11g	+ 0.0lg	+ 0.06g	+ 0.11g

The SPMDs actually gained some weight, and this can most likely be attributed to fouling of the membrane by algae and other aquatic organisms which were not all removed by cleaning of the SPMD.

In conjunction with the analysis of the triolein recovered from the SPMDs, a triolein spike was once again run to assure pesticide recovery was obtained through the extraction and clean-up procedure. Recovery of the pesticides from the Triolein Spike are given in Table 20.

Table 20. Pesticide Recovery in the Triolein Spike

Pesticide	**Spike Level (ug)**	**% Spike Recovery**
Trifluralin	1.0	85.0
Chlorpyrifos	10.7	100.0
Dieldrin	10.3	77.3
Atrazine	10.5	95.0
Furadan	10.0	85.0

Analysis of the SPMDs from four test sites at Don Williams Lake found no detectable levels of the 45 pesticides analyzed for in the test. Based on standard water analysis it would be likely to find only metolachlor and atrazine. However, these two compounds were not detected. Previous testing for these compounds in laboratory tests using SPMDs containing triolein showed poor recovery.

Considering their fairly good water solubility and moderate log Kow values, it would make it difficult to partition these compounds into triolein, especially at the low concentration levels that were found to be present in the lake water using standard water analysis methods.

CHAPTER 8. DISCUSSION OF RESULTS

In evaluating the use of semipermeable membrane devices as tools in analyzing pesticide concentrations in water, one must look at their use as a field monitoring device and as a laboratory testing device.

In the laboratory tests, SPMDs containing a solvent such as methylene chloride appear to be very effective in the analysis of a broad range of pesticides in water. A SPMD containing $MeCl_2$ demonstrated the ability to absorb high percentages of most pesticides. It is most ineffective in recovering pesticides with very low log Kow values and high water solubility, whether it be a triazine such as cyanazine, an organophosphate such as dimethoate or a carbamate such as carbofuran. Figure 13 shows a comparison between log Kow and pesticide recovery when $MeCl_2$ is used in the SPMD. Most pesticides with log Kow above 2.0 appear to be recovered fairly well. However, the recovery values for many of the organochlorines and pyrethroids appear low when considering their high log Kow values.

This low recovery of pesticides with high log Kows is probably due to a high percentage of absorption by the membrane matrix. This membrane absorption distorts the graph in the sense that it does not reflect pesticide removal from the water fraction and membrane retention. It would be reasonable to assume that some types of compounds such as pyrethroids and organochlorines that exhibit high log Kows would have a strong affinity for the nonpolar polyethylene membrane matrix, and this would result in poor recoveries in the $MeCl_2$ fraction. Also, this graph is only representative of $MeCl_2$ as the absorbing solvent, and the pesticide recovery patterns would change with different solvents depending on the polarity and solubility parameters of the solvent.

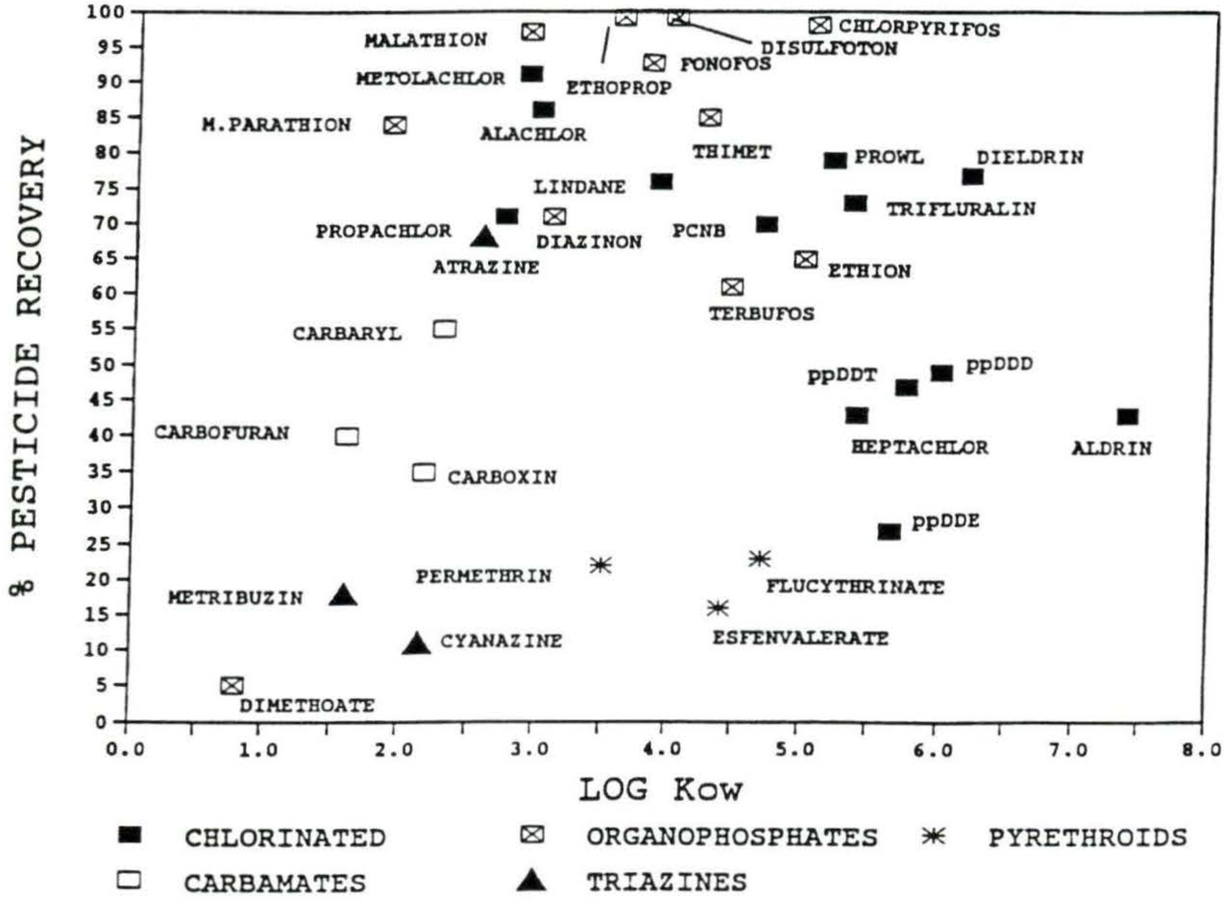

Figure 13. Recovery of pesticides from water by a SPMD containing MeCl2 Vs Log Kow. Exposure time = 24 hours

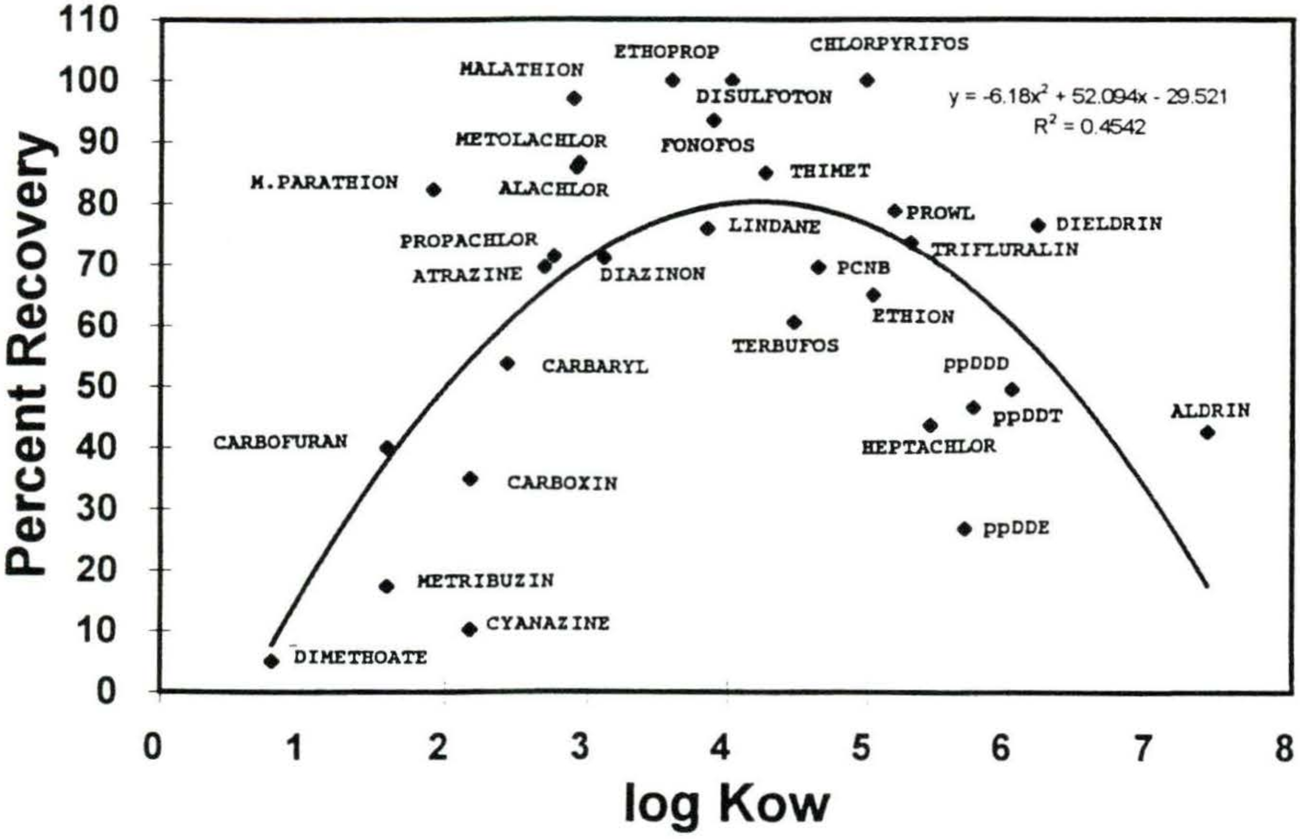

Figure 14. Relationship between pesticide recovery by a SPMD containing $MeCl_2$ and Log Kow with a superimposed theoretical recovery curve Exposure time = 24 hours

A direct linear relationship between pesticide recovered in the $MeCl_2$ fraction of the SPMD and log Kow is not immediately evident from recovery data plotted in Figure 13. However, pesticide recovery data does show a trend in which pesticide recovery in the $MeCl_2$ of the SPMD rises with increasing log Kow value to a point near the log Kow of 4. As log Kow rises beyond this point, recovery in the $MeCl_2$ fraction for the corresponding pesticides appears to decrease with increasing log Kow. This is especially evident when looking at the recovery of organochlorine pesticides, most of which have high log Kow values, but do not show the expected high recovery levels. It can be theorized that this decrease in $MeCl_2$ absorption of pesticides is the result of an increase in pesticide retention by the polyethylene membrane matrix. As log Kow rises, the corresponding compounds are becoming more and more nonpolar. As they become more nonpolar, they become more compatible with the membrane layer. This results in the absorption of the more nonpolar compounds by the membrane itself, and in a corresponding decrease in pesticide absorbed by the $MeCl_2$ in the SPMD. Although the pesticides are absorbed from the water fraction, a large portion is retained in the membrane rather than diffusing into the $MeCl_2$ within the SPMD. Figure 14 illustrates this trend as a theoretical curve superimposed over the data points that were plotted in Figure 13.

The trend line selected to best fit the data points is a second order polynomial curve whose equation is given in Figure 14. The line has a goodness of fit (R^2) of .4542 and a correlation coefficient (R) of .6739, indicating that the curve is a fairly good fit for the plotted data points.

In producing the trend line, the pyrethroid pesticides were omitted from the plot because their recovery appears to be affected to a greater degree by other factors besides Kow, such as molecular weight and size. Also, pyrethroid pesticides have been known to adhere to glass surfaces which could contribute to their lower recoveries when using a glass jar as a testing apparatus.

The relationship between log Kow and percent recovery for the chlorinated pesticides and dinitroanilines is shown in Figure 15. This figure shows that the chlorinated pesticides having a moderate log Kow values have good recovery, but as log Kow rises above 5.0 the percent recovery for all the corresponding pesticides, except dieldrin, declines. Once again, this is suggesting that the very nonpolar compounds are being absorbed by the membrane matrix.

Also, Figure 15 shows pesticides with similar structures grouping fairly close together, such as the chlorinated amides, propachlor, alachlor and metolachlor; as well as the dinitroanilines, trifuralin and pendimethalin (Prowl).

The recovery of organophosphates plotted against log Kow is shown in Figure 16. All of the organophosphate pesticides having moderate log Kow values (2.0 to 5.0) exhibit good recovery. The one organophosphate having a low log Kow (0.79) and being quite polar, dimethoate, is recovered very poorly (5.0%).

In addition to log Kow values, molecular weight and molecular size should also be considered as factors effecting pesticide absorption rate into the SPMD, since diffusion is limited by the pore size (5 to 10 Angstroms) existing in the membrane matrix. This would result in a more rapid absorption of smaller molecules and a slower absorption of larger molecules. The poor recovery of pyrethroid insecticides into the $MeCl_2$ of the SPMD could be due in part to their larger molecular weight which results in a reduced rate of diffusion across the membrane. Although high recovery levels would be expected for pyrethroids based on their high log Kow values, low recoveries are actually obtained because of the effects of high molecular weight and absorption by the membrane matrix.

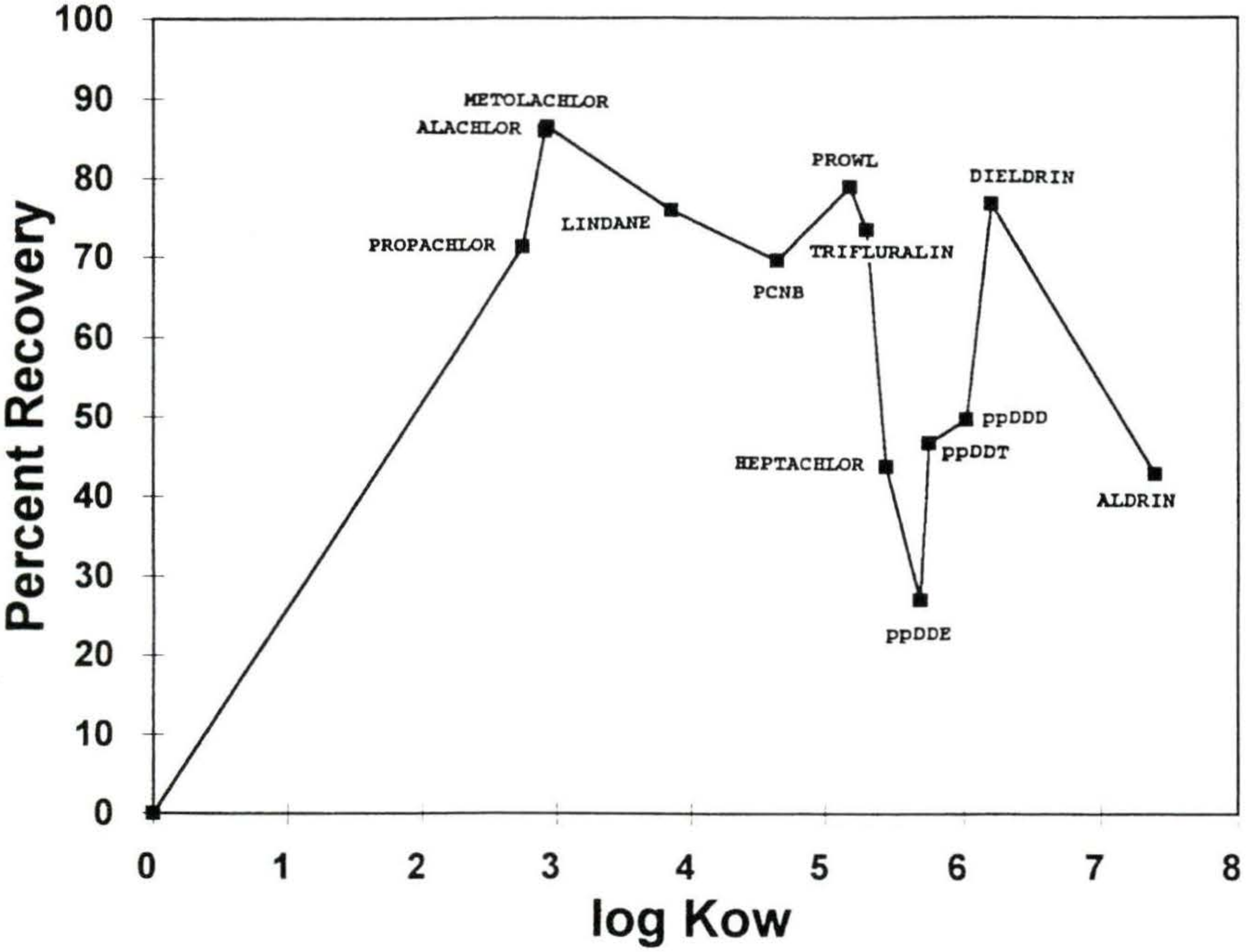

Figure 15. Percent recovery of chlorinated and dinitroaniline pesticides vs log Kow for a SPMD containing $MeCl_2$ in a 24-hr test

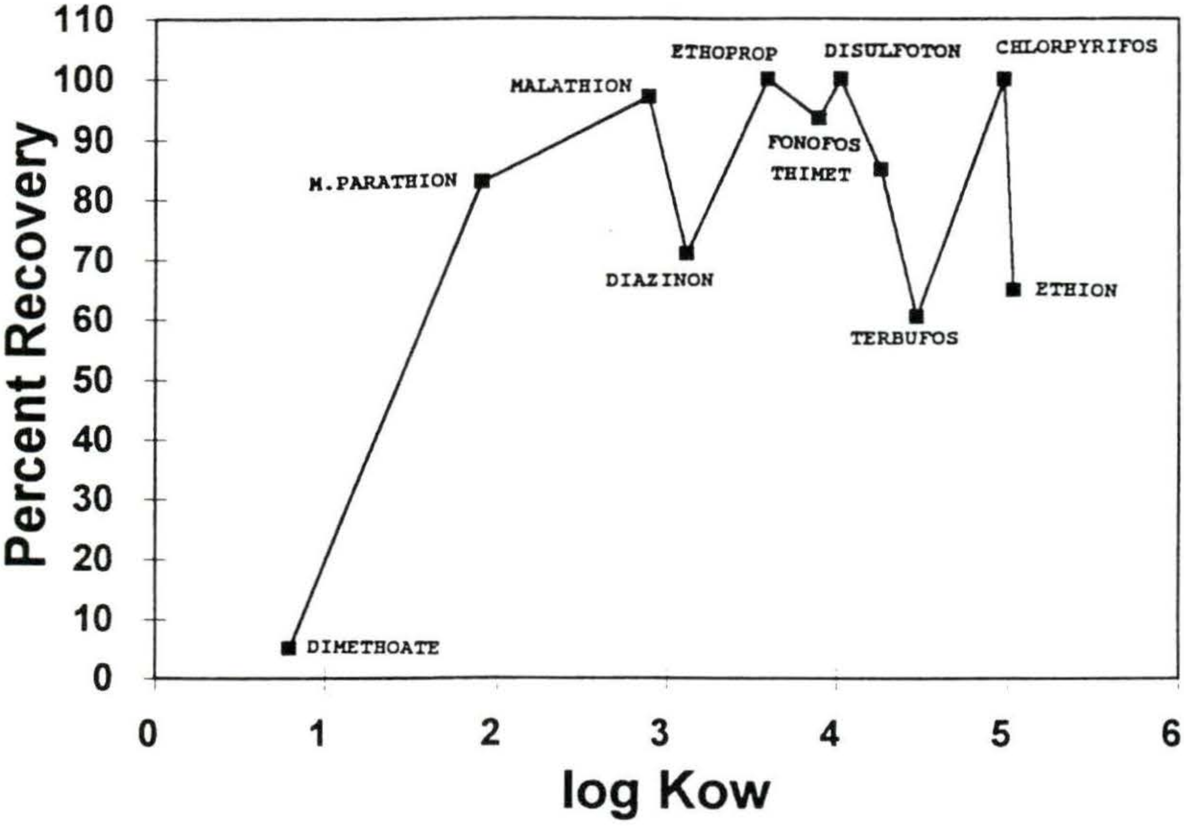

Figure 16. Percent recovery of organophosphate pesticides vs log Kow for a SPMD containing $MeCl_2$ in a 24-hr test

Based on the testing done in this work, it appears that SPMDs containing a solvent such as methylene chloride could have a practical application in the laboratory for the purpose of screening water samples for pesticide contamination. Twenty-four hour exposure tests could be run with a loss of about 20 ml per 100 ml of $MeCl_2$ used in the membrane device. A broad range of pesticides could be detected with this screening method. However, accurate quantitation of pesticide concentration in water would be difficult due to variable recovery rates for various pesticides and because of membrane retention of some pesticides. Standard methods for extraction of pesticides from water using $MeCl_2$ have the advantage over using solvent-filled SPMDs in the fact that they produce better recovery rates for most pesticides. The use of SPMD's for analyzing water may involve fewer extraction and clean-up steps than does standard extraction methods. However, the over-all extraction time would be longer due to the extended exposure time needed for the SPMD to absorb the pesticides from water. An exposure time of at least 24 hours would probably be necessary to reach an equilibrium state for most pesticides.

The test data suggests that SPMDs containing $MeCl_2$ could be used as a screening method in the laboratory to detect the presence of a great number of pesticides, but that standard extraction methods for water would be more effective in accurately quantitating pesticide concentrations in water.

SPMDs using triolein could be used in the laboratory to absorb some pesticides from water, but they would be less effective than using SPMDs containing $MeCl_2$. They appear to be ineffective in absorbing triazines, such as atrazine and cyanazine, as well as most carbamates. A comparison of Figures 8 and 11 shows that recoveries with $MeCl_2$ after 24 hour exposure was better than was the recovery of triolein after one week exposure time. Only chlorpyrifos was recovered at comparable rates. Atrazine and carbofuran recovery was much better using $MeCl_2$ in the SPMD. Also, when triolein is used, an extensive clean-up and extraction is necessary to remove the pesticides from the triolein for analysis. No cleanup is necessary using a solvent in the SPMD.

As a field monitoring device for absorbing pesticide contaminants in lakes and streams, a polyethylene membrane device containing $MeCl_2$ appears to be impractical because of the large loss of solvent from the membrane bag. In field studies, almost all of the $MeCl_2$ would diffuse from the membrane bag over an exposure period of 24 hours. Due to the nonpolar nature of the polyethylene membrane and the affinity of the low molecular weight solvents for the membrane, the solvents have a tendency to diffuse from the membrane device. This solvent loss can be reduced or eliminated by using polar non-porous membranes such as cellulose, but this results in a corresponding reduction in the absorption of nonpolar compounds from the surrounding water. (Sodergren, 1987; Johnson, 1991). Nonpolar membranes such as polyethylene appear to be most effective in the absorption of pesticide from water. However, they allow for the greatest solvent loss when $MeCl_2$ or more nonpolar solvents such as hexane are used in the SPMD.

SPMDs containing lipids such as triolein do not have this problem of diffusing through the membrane because of their large molecular size. Non-porous polymeric membranes such as polyethylene have channels or holes in the range of 5 to 10A° which limits the diffusion of the triolein molecule which has a length of 27A° and breadth of 28A° (molecular mass generally $\geq$ 600 Daltons) (Huckins et al. 1993). Triolein-containing SPMD can be deployed in lakes and streams for extended periods of time without significant triolein loss through the membrane. These devices have been shown to successfully partition nonpolar organic contaminants in water including pesticides such as DDT, mirex, trifluralin, chlordane, and fenvalerate (Huckins et al., 1991, 1993; Lebo et al., 1992; Prest et al., 1992). However, they have been most successful in absorbing the more nonpolar pesticides and do not appear to be effective in absorbing more polar compounds such as atrazine, cyanazine, metolachlor and carbamates such as carbofuran.

This would limit their used in monitoring water for pesticides, since it is the more polar, more water soluble compounds that tend to move more readily into our lakes, streams, and wells. The most commonly detected pesticides in water in the Midwestern United States include atrazine, metolachlor, cyanazine, simazine, alachlor, metribuzin, prometon, and 2,4-D (Goolsby et al., 1993a; Goolsby, et al., 1993b). Based on the studies, SPMDs containing triolein would not be very effective in absorbing most of these compounds which have fairly good water solubility and low to moderate log Kow values. Screening of water using SPMD's containing triolein could detect nonpolar pesticides such as dieldrin, chlorpyrifos, and trifluralin, but would most likely omit other more polar compounds such as atrazine, cyanazine, metolachlor, carbofuran, and metribuzin. This would limit their utility.

Although SPMDs containing triolein have been shown to have the ability to absorb many nonpolar contaminants from water in field tests, there still remains a problem in accurately quantitating contaminant levels in lakes and streams based on the contaminant concentration absorbed by the SPMD containing the lipid.

Huckins et al. (1992) have developed theoretical models for the prediction of water concentration of contaminants from absorbed lipid concentrations in the SPMDs. These models have been shown to be fairly accurate in their estimates of contaminant concentration when comparing estimated levels with measured water concentration levels for several contaminants. (Lebo et al., 1992, Huckins, et al., 1993). However, more work needs to be done to demonstrate the ability of SPMDs to function as quantitative monitoring devices for accurately measuring pesticide levels in aquatic environments.

Based on my experiments to evaluate the use of SPMDs for analyzing and monitoring water for pesticide contaminants, I have arrived at the following conclusions.

1. Solvent-containing SPMDs could be used as a tool to screen water samples for pesticides in the laboratory.
2. Solvent-containing SPMDs are more effective in absorbing a broad range of pesticides from water than are SPMDs using triolein.
3. Solvent-containing SPMDs made of polyethylene are ineffective in field monitoring tests because of the high rate of solvent loss through diffusion from the membrane into the surrounding water.
4. SPMDs containing triolein are more suitable for in situ monitoring of lakes and streams for pesticides than are solvent-containing SPMDs because loss of triolein is minimal even when deployed over long periods of time.
5. SPMDs containing triolein could be used to monitor water for many nonpolar organic contaminants including pesticides, but would be ineffective in absorbing many commonly used pesticides which have

higher water solubility and lower Log Kow values such as atrazine, cyanazine and carbofuran.

6. More studies must be performed to determine whether SPMDs can be used to accurately quantitate pesticide concentrations in water based on the concentration of absorbed contaminants.

Additional work needs to be performed to evaluate the use of SPMDs for the purpose of monitoring pesticide residues in water. The following studies involving the use of SPMD for pesticide analysis are recommended:

1. Evaluation of a variety of polymers as membrane materials for the purpose of finding a membrane that is effective in reducing solvent loss from diffusion, and is still capable of absorbing pesticides from water.
2. Examine additional absorbent materials which could be used as alternatives to triolein and organic solvents inside the SPMD membrane.
3. Develop a SPMD configuration that is effective in absorbing the more polar pesticides such as carbamates and triazines from water.
4. Perform laboratory tests with SPMDs to determine if pesticide concentration in spiked water samples can be accurately predicted from the measured concentration of pesticide found within the SPMD by using equations similar to those developed by Huckins et al. (1992) at the U.S. Fish and Wildlife Service in Columbia, MO.
5. More intensive time studies need to be performed extending the time exposure beyond 24-hours. Individual pesticides must be analyzed over longer periods of time using multiple replicates to accurately

determine the time of equilibrium for each compound as well as the percent recovery level reached at this equilibrium point.

6. Additional analysis needs to be performed with selected pesticides in 24-hr recovery tests using solvent and lipid containing SPMDs. Studies using a greater number of replicates are necessary to better determine average recovery of pesticide after 24 hours of exposure and the degree of variation that exists in the testing. Multiple replicates would allow for statistical evaluation of the reproducibility of the recovery values for each pesticide tested.

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APPENDIX 1

Total acres planted and percentage of acres treated with herbicides and insecticides. (Iowa State University Extension 1991)

				% Acres Treated					
	Acres planted (1,000)			Herbicides			Insecticides		
Crop	1979	1985	1990	1979	1985	1990	1979	1985	1990
Corn	13,500	13,900	12,800	95	97	95	50	43	35
Soybeans	8,200	8,200	8,000	97	97	97	*	*	0.4

*Data not available

APPENDIX 2

Major herbicides used in Iowa Corn production. (Iowa State University Extension, 1991)

	1979		1985		1990	
Herbicide	% acres	lb.a.i.* (1,000)	% acres	lb.a.i.* (1,000)	% acres	lb.a.i.* (1,000)
alachlor	40.7	11,357	33.7	9,900	22.3	6,245
atrazine	32.9	6,642	49.0	9,716	61.0	7,548
bentazon	NR	-	0.2	25	2.5	147
bromoxynil	NR	-	3.0	250	17.2	577
butylate	29.7	13,597	8.9	3,958	0.7	291
cyanazine	32.7	8,513	33.9	10,366	19.6	5,120
dicamba	19.4	832	20.3	774	20.6	817
EPTC	0.6	381	0.8	489	13.2	7,389
linuron	0.2	24	0.4	44	0.0	0
metolachlor	4.6	1,535	37.2	10,343	34.4	9,403
pendimethalin	0.4	98	0.3	50	3.1	535
Propachlor	4.2	1,714	2.7	1,126	2.3	558
2,4-D	18.2	1,154	18.9	788	14.4	805
Total pounds a.i.		45,847		47,829		39,435

NR - Not registered
a.i. = Active ingredient

APPENDIX 3

Major herbicide used in Iowa soybean production (Iowa State University Extension Exchange, 1991)

	1979		1985		1990	
Herbicide	% acres	lb. a.i. (1,000)	% acres	lb. a.i. (1,000)	% acres	lb. a.i. (1,000)
aciflourfen	-	-	0.8	13	6.7	115
alachlor	29.1	4,224	12.3	2,119	9.8	1,557
bentazon	5.6	459	13.9	798	20.6	1,191
bifenox	2.6	551	0.3	44	NR	-
CIPC	306	3.6	0.2	31	NR	-
chloramben	13.8	1,606	13.0	1,386	1.8	131
chlorimuron	NR	-	NR	-	20.1	17
clomazone	NR	-	NR	-	13.3	730
ethalfluralin	NR	-	7.0	517	8.5	566
fenoxaprop	NR	-	NR	-	0.3	3
fluazifop	NR	-	0.5	12	6.0	65
glyphosate	0	0	13.0	213	8.0	171
imazaquin	NR	-	NR	-	1.4	12
imazethapyr	NR	-	NR	-	21.4	88
lacatofen	NR	-	NR	-	0.7	12
linuron	4.4	325	1.9	109	0.4	21
metolachlor	0.6	139	7.8	1,472	3.5	578
metribuzin	40.8	1,594	43.0	1,763	11.00	300
pendimethalin	1.0	89	5.4	487	8.9	825
quiaziflop	NR	-	NR	-	6.2	34
sethoxydim	NR	-	1.4	23	7.0	116
trifluralin	60.8	4,535	63.2	4,664	55.0	3,657
2,4-DB	0	0	0.5	4	2.4	20
Total pounds a.i.		13,888		13,442		10,038

NR - Not registered
a.i. = Active ingredient

APPENDIX 4

Insecticides used in Iowa corn production (Iowa State University Extension, 1991)

	1979		1985		1990	
Insecticide	% acres	lb. a.i.[1] (1,000)	% acres	a.i.[2] (1,000)	% acres	1b. a.i.[1] (1,000)
carbofuran	8.9	1,135	2.9	449	1.1	170
chlorpyrifos	4.6	670	11.5	1,817	7.5	1,085
disulfoton	0	0	0	0	0.2	8
ethoprop	2.8	343	0.2	33	0	0
fenvalerate	0	0	1.6	23	0	0
fonofos	11.5	1,633	7.0	968	4.0	430
heptachlor	0.1	6	NR	-	NR	-
malathion	0	0	0	0	0.3	55
permethrin	NR	-	2.4	33	1.0	12
phorate	7.1	993	4.7	774	2.9	434
teflluthrin	NR	-	NR	-	0.8	11
terbufos	16.2	2,300	13.2	2,195	17.9	2,591
toxaphene	0.1	63	NR	-	NR	-
Trimethacarb	NR	-	0.4	51	0.1	15
Total pounds a.1.		7,143		6,343		4,811

[1] Reported rate

[2] Estimated rate

NR = Note registered

a.i. = Active ingredient

APPENDIX 5

Summary of the Iowa State-wide RuralWell-waterSurvey: June, 1991, Water-quality Results for Pesticides (Iowa Department of Natural Resources, 1993.)

	All Wells	Wells <50ft	Wells >=50ft
Pesticides:			
% sites with any pesticides detection	19.8%	22.5%	14.1%
Atrazine (parent)			
% sites with detection	6.0%	0.0%	7.5%
mean conc., ug/L	0.6	0.0	0.8
max conc., ug/l	0.9	0.0	0.9
HAL* ug/L	3.0	3.0	3.0
De ethyl atrazine			
% sites with detections	4.8%	5.0%	2.3%
mean conc., ug/L	0.6	0.8	0.6
De Isopropyl atrazine			
% sites with detections	4.0%	0.0%	4.6%
mean conc., ug/L	0.4	0.0	0.3
Total Atrazine			
% sites with detections	10.5%	5.0%	7.6%
mean conc., ug/L	0.7	0.8	0.9
max conc., ug/l	2.0	0.8	2.0
Alachlor (lasso)			
% sites with detections	1.8%	5.0%	0.0%
mean conc., ug/L	0.2	0.2	0.0
max conc., ug/l	0.2	0.2	0.0
HAL ug/L	0.4	0.4	0.4
hydroxy alachlor			
% sites with detecton	2.7%	5.9%	0.0%
mean conc., ug/L	2.4	1.7	0.0
Metolachlor (Dual)			
% sites with detections	8.1%	5.0%	6.5%
means conc., ug/L	20.4	151.0	1.9
max conc., ug/l	151.0	151.0	2.7
HAL ugL	100.0	100.0	100.0
Metribuzin (Sencor)			
% sites with detections	3.0%	5.6%	2.3%
mean conc., ug/L	0.03	0.04	0.03
max conc., ug/l	0.04	0.04	0.03
HAL ug/L	200.0	200.0	200.0
Trifluralin (Treflan)			
% sites with detections	3.50%	5.6%	0.0%
mean conc., ug/L	0.02	0.02	0.0
max conc., ugl/l	0.03	0.03	0.0
HAL ug/L	2.0	2.0	2.0

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* Health Advisory Level

APPENDIX 6

Frequency of pesticide and pesticide metabolite detections in water from wells sampled during 1992, Midcontental United States (Kolprin et. al., 1993)

(1ug/L, micrograms per liter; ESA. alachlor metabolite)

Compound	percent detection	Number of samples[1]	Maximum concentration (1up/L)	Reporting limit (1up/L)	Action/use[2]
Any pesticide or metabolite	62.0	100			
ESA	47.0	66	4.95	0.100	Herbicide Metabolite (Alachlor)
Atrazine	43.0	100	1.03	.005	Selective herbicide: corn, sorghum
Deethylatrazine	31.0	100	1.79	.015	Herbicide metabolite (atrazine)
Deisopropylatrazine	18.2	66	.28	.050	Herbicide metabolite (alachlor)
2,6-Dietylanaline	16.0	94	.022	.003	Herbicide metabolite (alachlor)
DCPA	15.6	45	2.22	.010	Herbicide metabolite(dacthal)
Simazine	13.0	100	.077	.005	Selective herbicide: corn,
Metolachlor	11.0	100	.76	.002	Selective herbicide:corn,sorghum,soybeans
Prometon	9.0	100	1.35	.010	Nonselective herbicide
2,4-D	6.7	45	.89	.010	Selective herbicide: corn, sorghum, pasture
P,P' DDE	6.4	94	.03	.006	Insecticide metabolite (DDT)
Alachlor	5.0	100	.99	.002	Preemergent herbicide: corn soybeans
Dicamba	4.4	45	.01	.010	Herbicide
Pichloram	4.4	45	.03	.010	Systemic herbicide:deep-rooted plants
Chlorpyrifos	4.2	94	.024	.004	Insecticide: corn, soybeans
Ethalfluralin	3.2	94	.014	.004	Selective preemergence herbicide: soybeans
Cyanazine	3.0	100	.02	.008	Selective herbicide: corn
2,4,5-T	2.2	45	.02	.010	Discontinued herbicide
EPTC	2.1	94	.003	.002	Selective herbicide: corn
Trifluralin	2.1	94	.016	.003	Selective preemergence herbicide: soybeans
Triallate	2.1	94	.007	.001	Selective preemergence herbicide: wheat
Benfluralin	1.1	94	.018	.004	Herbicide: alfalfa, clover
Napropamide	1.1	94	.008	.003	Selective herbicide: orchards, tobacco
Pendimethalin	1.1	94	.01	.008	Selective herbicide: corn, soybeans
Propachlor	1.1	94	.002	.007	Herbicide
Tebuthiuron	1.1	94	.05	.010	Herbicide: noncropland areas, rangeland
Metribuzin	1.0	100	.05	.005	Herbicide: soybeans

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[1] When sample size is less than 94, the frequency of detection for that compound may be affected by the biased sample selection toward wells that had a herbicide detection during 1991

[2] modified from Meister (1992)

APPENDIX 7

Pesticides in water supplies using surface water sources. Analytical results comparing treated (F-finished) and Untreated (R-raw) water samples for sites in Iowa (Wnuk et. al., 1987)

Analytical Result Comparing Treated (F-finished and Untreated (R-raw Water Samples (1 ug/l or ppb)

Water Supply Name		atrazine	cyanazine (Bladex)	metolachlor (Dual)	alachlor (Lasso)	metribuzin (Sencor)	carbofuran (Furadan)	2,4-D	dicamba (Banvel)
Albia	R	1.1	1.4		0.21		1.8		
	F	0.97	1.2		0.24			N.A	N.A
*Bedford	R	0.47	0.12						
	F	0.59	0.13						
Clarinda	R	0.97	0.31	0.46					
	F	0.72	0.55	0.26					
Council Bluffs	R								
	F								
Davenport	R	0.24		0.1	0.23				
	F	0.18							
*Des Moines	R	0.47	0.44	1.2	.0.98		0.72		
	F	0.34	0.29	0.69	0.59		0.38		
*Fort Madison	R	21.0	14.0	5.5	5.1	0.89	14.0	N.A	N.A
	F	6.0	4.6	1.7	1.7	0.28	4.7		
Humeston	R	26.0	20.0	10.0	0.13		17.0	.17	1.2
	F	24.6	17.0	8.3	0.16		14.0		1.4
Lakeview	R	0.18							
Heights	F	0.2							
Orient	R	1.9		1.0					
	F	0.60		0.3					
Ottumwa	R	0.88	0.57	0.72	0.28				
	F	0.71	0.46	0.51	0.29				
Panora	R	0.56	0.42	0.69	0.43				
	F	0.46	0.35	0.46	0.41				
Rathbun RWA	R	2.2	0.50	0.68	0.14				
	F	1.8	0.62	0.37					
University of Iowa	R	12.0	3.2	9.8	9.3		2.0	.15	
May 18, 1986	F	15.0	7.2	10.0	8.8	0.31	1.2	.15	
May 19, 1986	F	12.0	5.4	7.8	7.8	<0.1	6.0	N.A.	

N.A. = Not Analyzed

R - Raw (Untreated) Water

*These facilities have more than one permanent untreated water source and finished water may be a blend.

APPENDIX 8

List of Pesticide Standards Used In Testing

Alachlor (Lasso), 99.0% Purity (Chem Serve)

Aldrin, Analytical, 99.5% (Shell Chemical)

Alpha BHC, 98% (EPA Reference, Triangle Park, N.C.)

Atrazine, 98% Purity (Chem Serve)

Butylate (Sutan), 99.8% (ICI Americas, Inc.

Carbaryl (Sevin), 99.5%, Tech Grade (Rhone Poulene)

Carbofuran (Furadan) 99.0%, Analytical, (FMC Corp.)

Carboxin, 100%, (EPA Ref.)

Chlorpyrifos (Dursban), 97.5% (EPA Ref.)

Cyanazine (Bladex), 99.8%, (Ultra Scientific)

DCPA (Dacthal), 99.0% (Ultra Scientific)

Diazinon, 96.7%, Tech. Grade (Iowa State University, Vet. Diag. Lab)

pp DDE, 99% Analytical, (Chem Serve)

op DDD, 99+%, (EPA Ref.)

pp DDD, 98%, (Chem Serve)

op DDT, 99+%, (EPA Ref.)

pp DDT, 99.5%, (EPA Ref.)

Dieldrin, 99.5%, (EPA Ref.)

Dimethoate, 99.8%, (EPA Ref.)

Disulfoton (Disyston), 97.0%, Tech Grade, (EPA ref.)

EPTC (Eradicaine), 99.8%, (ICI Americas Inc)

Esfenvalerate (Asana), 99.9% (Dupont de Nenoirs, Inc)

Ethion, 95%, (EPA Ref.)

List of Pesticide Standards Used In Testing (continued)

Ethroprop (Mocap), 98.4%, (EPA Ref.)

Fenvalerate (Pydrin), 95%, Tech, Grade, (Dupont de Nenoirs, Inc)

Flucythrinate, 93.9%, (EPA Ref.)

Fonofos (Dyfonate), 93%, Analytical, (Chem Serve)

Heptachlor, 99.9%, (EPA Ref.)

Lindane, 99.86% (EPA Ref.)

Malathion, 99.9% Analytical, (American Cyanamid)

Maneb, 89.2%, (EPA Ref.)

Methyl Parathion, 98.3%, Analytical, (EPA Ref.)

Metolachlor (Dual), 96.0%, (Chem Serve)

Metribuzin (Sencor), 100%, (EPA Ref.)

Nitrapyrin, 99.6%, (Ultra Scientific)

Oxyflourfen (Goal) 99.7%, (EPA Ref.)

PCNB (Pentachloronitrobenzene), 99.0% (EPA Ref.)

Cis-Permethrin (Ambush), 99.2% Analytical (FMC Corp.)

Trans-Permathrin (Ambush), 99.2% Analytical (FMC Corp.)

Pendimethalin (Prowl), 99.9%, (Ultra Scientific)

Phorate (Thimet), 97%, (American Cyanamid)

Propachlor (Ramrod), 99.9%, (EPA Ref.)

Terbufos (Counter), 95%, Tech. Grade, (EPA Ref.)

Thifensulfuron Methyl (Harmony), 99.62% (Dupont de Nemoirs, Inc)

Trifluralin (Treflan), 98.0% (EPA Ref.)1

APPENDIX 9

Log Kow and Water Solubility Values for Selected Pesticides

Pesticide	Molecular Weight	Log Kow	Water Solubility at 25°C (ppm's)
Dimethoate	229.28	.79[a]	25,000[b]
Dichlorvos	220.98	1.39[b]	10,000[b]
Simazine	201.67	1.51[b]	3.5[b]
Aldicarb	190.25	1.57[a]	7,800[b]
Carbofuran	221.26	1.60[b]	700[j]
Metribuzin	214.28	1.60[h]	1220(at 20°C)[i]
Methyl Parathion	263.26	1.91[b]	57[b]
Diuron	233.10	1.97[b]	42[b]
Cyanazine	240.68	2.17[b]	171[i]
Carboxin	255.31	2.17[h]	170[h]
Linuron	249.11	2.18[b]	75[b]
Methomyl	162.20	2.20[b]	10,000[b]
Picloram M.E	255.51	2.30[a]	430[b]
Carbaryl	201.22	2.32[a]	40[b]
Bentazon	240.28	2.34[b]	500[b]
EPTC	189.31	1.38[b]	365[b]
Captan	300.57	2.54[a]	0.5[b]
Atrazine	215.68	2.68[b]	33[i]
Propachlor	211.69	2.75[b]	580[b]
Propanil	218.09	2.80a	225[j]
2,4-D	221.04	2.81[e]	900[b]
Phosmet	317.32	2.83[b]	25[b]
Malathion	330.36	2.89[b]	145[b]
Propazine	230.09	2.89[b]	8.6[b]
Alachlor	269.77	2.91[b]	242[i]
Metolachlor	283.81	2.93[h]	530(at 20C)[i]
Chlorfenvinphos	359.56	3.10[a]	145[j]
Diazinon	304.36	3.11[a]	40[b]
2,4,5-T	255.49	3.13[e]	238[b]
Fenamiphos	303.36	3.18[a]	329[j]
Fenitrothion	277.25	3.38[b]	30[b]
Nitrapyrin	230.93	3.41[b]	40[b]
Prometryn	225.29	3.46[e]	48[b]
Permethrin	391.29	3.48[f]	0.2(at 30°C)[k]
Ethoprop	242.32	3.59[h]	750[j]
Folpet	296.58	3.63[a]	60[a]
Hept. Epoxide	389.32	3.65[h]	.275[h]
Dinoseb	240.22	3.69[a]	50[b]
Amiben M.E.	270.05	3.80[a]	120[b]
Captafol	349.09	3.83[a]	60[a]
Lindane	290.85	3.85[d]	.15[b]
alpha BHC	290.85	3.85[d]	.15[b]

Log Kow and Water Solubility values for Selected Pesticides (continued)

Pesticide	Molecular Weight [j]	Log Kow	Water Solubility at 25%C (ppm's)
Fonofos	246.32	3.89[h.i.]	13[k]
Ethyl Parathion	291.27	3.93[a]	24[b]
Disulfoton	274.38	4.02[i]	25[b]
Phorate	260.40	4.26[a]	25[k]
Methoxychlor	345.65	4.30d	.003[b]
Fenvalerate	419.92	4.42[f]	1.0[k]
Terbufos	288.41	4.47[i]	12[b]
PCNB	295.36	4.64[g]	.6[a]
Flucythrinate	451.48	4.70[h]	.5[h]
Chlorpyrifos	350.57	4.98[b]	2.0[b]
PCP	266.35	5.01[d]	80[j]
Ethion	384.48	5.03[i]	2.0[b]
Pendimethalin	281.31	5.18[h]	.3(at 20°C)[j]
HCB	284.80	5.22[b]	.035[b]
Trifuluralin	335.29	5.30[b]	.6[b]
Endrin	380.93	5.34[b]	.024[b]
Heptachlor	373.35	5.44[d]	.030[b]
ppDDE	318.04	5.69[d]	.010[b]
ppDDT	354.50	5.75[d]	.0017[b]
opDDT	354.50	5.75[d]	.0017[b]
Chlordane	409.80	6.00[d]	.056[b]
ppDDD	320.05	6.02[b]	.005[b]
Dieldrin	380.93	6.20[a]	.022[b]
Arochlor 1254	-	6.47[d]	.01[b]
TCDD	-	6.90[a]	.06[a]
Aldrin	364.93	7.4[a]	.013[b]
Mirex	545.59	7.5[c]	.60[b]

References

a. Briggs (1981)
b (Kenaga and Goring)(18)
c. Gobas and Mackay (1987)
d. Mackay (1982)
e. Somasundarum, Coats, and Racke (1991)
f. Coats and O'Donnel-Jeffrey (1979)
g. Howard (1991)
h. Montgomery (1993)
i. Weed Science Society of America (1983)
j. Merck Index (1989)
k. Worthington C.R. ed. (1983)
i. Bowman and Sons (1983)