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Stability of Various Pesticides on Membranous Solid-Phase Extraction Media

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■ The stability of various pesticides in water at 4 °C was compared with their stability on C-18 SPE disks under three storage regimes. The disk storage regimes involved using the disk to extract the chemical from water, removing the disk and placing it in a plastic bag, and then storing it at either −20 or +4 °C for 1 day and then −20 °C for the remainder of the storage period. The storage periods included 0, 3, 30, 90, and 180 days. The percent recovery of each chemical was determined and used to compare storage treatments. Results indicate that the pesticides have equivalent or greater stability on solid-phase extraction disks compared to their storage in water at 4 °C. The data suggest that freezing the disk after pesticide loading is the most favorable storage option. Results show that field extraction/storage methodology is feasible, which could improve the reliability of future environmental water sampling procedures.

Introduction

Sample stability and storage space are problems that many environmental laboratories must address when collecting, storing, and analyzing water samples. Two significant means by which pesticides in water degrade are hydrolysis and microbial decomposition. Compounds such as captan are known to degrade rapidly in water (*4*). With the large numbers of samples typical of environmental studies, the use of bulky glass bottles for sampling, transport, and storage also becomes a hindrance. Solid-phase extraction (SPE) technology is a growing area of research in the development of environmental sample preparation. Early applications of SPE techniques in the form of cartridges have provided equivalent recoveries when compared to liquid/liquid extraction techniques (*3*). More recently, advanced SPE technology has resulted in SPE membrane filters or filter disks. The unique design of the disk provides desirable properties previously unattainable by SPE cartridges (*2, 3*). The disks used in our experiment consist of a Teflon fibril network embedded with 18-carbon (octadecyl) hydrocarbon chains bonded to silica particles (Figure 1).

As a sample is filtered through the disk, the nonpolar C-18 chain or hydrocarbon acts as a partitioning solvent for most of the nonpolar organic compounds while the highly polar water passes through. Presently, the stability of pesticides stored on SPE disks is not known. Studies with SPE cartridges have demonstrated increased stability of other hydrocarbons when attached to the organic matrix (*1*). The hypothesis is that the stability of certain pesticides may be improved due to protection from hydrolysis and microbial decomposition when pesticides are adsorbed on SPE disks. The objectives of the study were (1) to compare the relative storage stability of selected pesticides on SPE disks to the storage stability of pesticides in water and (2) to determine the chemical stability of the selected pesticides on the extraction disks under various temperature/storage regimes over time.

Experimental Section

Analytical Methodology. All samples were coidentified and quantified by gas chromatography (GC) and high-performance liquid chromatography (HPLC). Compounds determined by GC were analyzed by a Shimadzu GC-14A equipped with an electron capture detector (ECD). The injected sample was split to two columns, each 0.53 mm × 15 m containing SPB-5 and SPB-608 stationary phases, respectively. The temperature program was 180 °C for 2 min, increased at 1 °C/min to 190 °C for 0 min, and increased at 2 °C/min to 220 °C for 7 °C/min. Injector and detector temperatures were 250 and 300 °C, respectively. The flow rate through the column was 4 mL/min.

HPLC analyses used an Isco 2250 UV variable-wavelength detector set at 225 nm with sensitivity set at 0.05 absorbance units full scale (AUFS). The mobile phase used through the C-18 Partisphere column was a 40% methanol, 45% deionized water, and 15% pH 7 buffer mixture at a flow rate of 2 mL/min. The pH 7 buffer was made by mixing 244 mL of 0.067 M Na_2HPO_4 plus 156 mL of 0.067 M KH_2PO_4. The retention times and method of detection for each compound studied are shown in Table I.

Each water sample was fortified at 20 μg/L with the respective pesticides. The form of solid-phase extraction used was the Empore disks for environmental analysis, 47-mm diameter (3M Industrial and Electronic Sector, New Products Department, St. Paul, MN 55144-1000, distributed by Varian Sample Preparation Products, 24201 Frampton Ave., Harbor City, CA 90710).

Experimental Design. A completely randomized design with four replications employed a factorial arrangement of four storage treatments and five time periods. The treatments used in this study represented several different conditions of pesticide storage. The four storage treatments included (1) bottled water stored at 4 °C, (2) pesticides stored on SPE disks at 4 °C, (3) pesticides stored on SPE disks at −20 °C , and (4) a combination treatment (4 °C for 1 day and then −20 °C for the remainder of the storage period). The rationale behind the various treatments was to represent the accepted method for sample storage (bottled water in amber glass jars stored at 4 °C) and several alternatives to the accepted method by storage

Table I. Retention Times of Compounds Quantified in Storage Study

compound	retention time, min: GC-ECD SPB-5 column	GC-ECD SPB-608 column	HPLC-UV C-18 column
alachlor	5.1	6.1	ND[a]
atrazine	ND	ND	8.4
benomyl	ND	ND	2.5
captan	7.9	14.7	ND
fluometuron	ND	ND	7.1
methyl parathion	4.8	7.1	18.5
metolachlor	5.9	8.4	ND
norfluorazon	16.9	24.9	ND
pendimethalin	6.5	10.7	ND
profenofos	11.0	15.9	ND
simazine	ND	ND	4.5
trifluoralin	2.5	2.2	ND

[a] ND, not determined.

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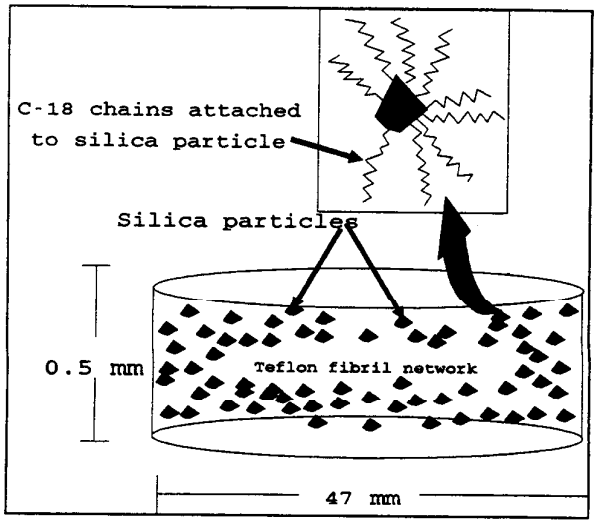

Figure 1. Model of solid-phase extraction disk.

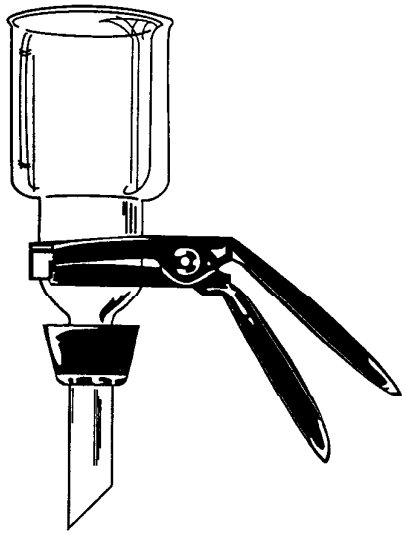

Figure 2. Sintered glass filter funnel used for solid-phase extraction of pesticides from water.

on C-18 material that represent various temperatures and combinations of temperatures. The disk treatment stored at 4 °C is a direct temperature comparison for pesticides stored in water at the same temperature. The frozen disk treatment represents what one assumes would be the most optimum temperature to store the pesticides on the disk in a routine laboratory and would also offer flexibility to the laboratory that is not always prepared to immediately analyze all samples upon their arrival. The combination treatment depicts a practical application of pesticide disk storage if one were to extract the pesticides in the field. In this case, the pesticides would be concentrated on the disk and then the disk would be stored in a plastic bag and kept on ice until transported back to the laboratory, where it would be frozen.

The five storage periods were 0, 3, 30, 90, and 180 days. Percent recoveries of the original pesticide concentrations in water were recorded. Means of percent recovery were calculated and separated by Fisher's protected least significant difference (LSD) at a 0.05 level of significance (SAS, Statistical Analysis Systems, Carey, NC).

Extraction Procedure. Treatments were separated into two groups: (1) bottle storage and (2) disk storage. The bottle storage samples were prepared by placing 250 mL of deionized water in an amber glass jar and fortifying the water with the pesticide mixtures dissolved in an organic solvent. All pesticides added to the fortification solution were dissolved in methanol with the exception of captan, which was dissolved in benzene. Captan was treated in this manner because it was found to be unstable in methanol. Thus, a 2500 μg/mL concentration of captan in benzene allowed fortification with a small quantity of the benzene solution, such that the concentration of benzene in solution would not elute compounds from the disk upon extraction or cause layering in the water solution.

Preparation of disk storage samples involved fortification of water samples as indicated above and then extraction of the pesticides onto the disk.

Extraction of Pesticides onto the Disk. A volume of 250 mL of deionized water was measured and placed in a 250-mL Erlenmeyer flask. Two milliliters of methanol, 1.0 mL of fortification solution, and 2 μL of the prepared captan solution were added to the water sample, producing a 20 μg/L concentration of each pesticide in water. An Empore extraction disk was placed on a sintered glass filter funnel apparatus attached to a vacuum source (Figure 2).

Ten milliliters of a 1:1 methylene chloride/ethyl acetate solvent was added to the filter funnel and the solvent drawn through the disk at a rate of approximately 10 mL/5 s. Subsequently, air was drawn through for 1 min. Methanol (10 mL) was then added. As the solvent was drawn through, the vacuum was removed when a film of methanol covered the disk. This prevented drying and subsequent slow filtration. Deionized water (10 mL) was added to the thin film of methanol and drawn through until a thin film of deionized water covered the disk; the vacuum was again removed. The entire fortified sample (250 mL) was then added to the filter funnel and drawn through at approximately 25–30 mL/min. After the sample had been drawn through, the vacuum was left on for 5 min to allow the disk to dry. The disk was removed from the filter holder, placed in a plastic sandwich bag, and stored under the appropriate regime.

Extraction and Preparation of Stored Pesticides for Analysis. After storage, the filter was visibly reoriented back on the filter apparatus so that the originally exposed area was above the sintered glass. Borosilicate glass vials (20-mL capacity) were then placed in the base of the vacuum manifold to catch the eluate. The pesticides were eluted from the disks with 2 × 5 mL of ethyl acetate. During each application of ethyl acetate, the vacuum was applied and removed quickly to allow some of the ethyl acetate to penetrate the entire thickness of the disk for an equilibration time of 2 min. The vacuum was then reapplied, and the remainder of the ethyl acetate was eluted into the glass vials. Anhydrous sodium sulfate (3 g) was added to the vial to remove any excess water. The ethyl acetate was decanted into a calibrated test tube. The glass vials were rinsed three times with ethyl acetate, each time decanting into the calibrated test tube. The final volume was brought to 5 mL of ethyl acetate by a stream of dry nitrogen with the vials immersed in a 30–35 °C water bath. A 1.5-mL aliquot of the sample was placed into a sample vial for GC analysis. The remaining 3.5 mL of sample was brought to dryness and then redissolved with the HPLC mobile phase to a 3.5-mL final volume. A 1.5-mL aliquot was taken for HPLC analysis.

Freshly fortified samples were concomitantly extracted with each batch of storage treatments to ensure that the efficiency of the analytical procedure was consistent. Also, solvent-washed disks were stored with each storage regime

Table II. Effect of Storage Treatment on Percent Recovery of Benomyl, Simazine, Fluometuron, and Atrazine Averaged over All Storage Periods

treatment	% recovery[c] benomyl	simazine	fluometuron	atrazine
disk stored,[a] 4 °C	68	65	74	70
disk stored,[a] −20 °C	76	71	79	75
disk stored,[a] 4 °C, −20 °C	70	69	76	70
bottle stored,[b] 4 °C	63	61	67	64
LSD (0.05)[d]	5.4	6.1	3.8	4.6

[a] Pesticide/water solutions filtered and vacuum-dried through C-18 disks. [b] Pesticides stored in bottles containing 250 mL of water. [c] Mean values obtained from 20 observations. [d] Least significant difference. If the difference between the two compared values is greater than the LSD, the values are considered to be statistically similar. If the difference is smaller than the LSD, the values are statistically similar.

Table III. Effect of Storage Time on Percent Recovery of Benomyl, Simazine, Fluometuron, and Atrazine Stored on C-18 Disks Averaged over All Disk Storage Treatments

storage period (days)	% recovery[a] benomyl	simazine	fluometuron	atrazine
0	75	79	86	79
3	85	86	86	85
30	79	68	74	72
90	60	44	66	55
180	60	64	71	67
LSD (0.05)[b]	7.0	8.1	4.7	6.0

[a] Mean values obtained from 12 observations. [b] Least significant difference. If the difference between the two compared values is greater than the LSD, the values are considered to be statistically similar. If the difference is smaller than the LSD, the values are statistically similar.

for analysis as blanks (no pesticide fortification).

Results and Discussion

Benomyl, simazine, fluometuron, and atrazine showed no interaction between storage treatment and storage period (Tables II and III). In general, the highest percent recovery for these pesticides occurred when the disk was stored at −20 °C and the lowest recovery on the disks occurred at 4 °C, although these recoveries did not always differ statistically. In all cases, each pesticide stored at −20 °C on the C-18 material gave better recovery than those stored in bottled water (Table II). Moreover, the lowest recovery was for the pesticides stored in bottled water, but it was not always statistically different from the next lowest value within a selected disk storage treatment. The combination treatment gave the second highest percent recovery for each pesticide. Simazine showed no differences among disk storage treatments, indicating that temperature had no effect on the recovery of this compound. Statistical differences in recovery from disks were shown for benomyl, fluometuron, and atrazine out of these four compounds (Table II). Thus, consistent differences in percent recovery did not occur between specific disk storage treatments among these pesticides. Nevertheless, these data show that these pesticides are at least as stable and often more stable as compared to those stored in water over the same duration (Table II).

Since the storage stability of pesticides on SPE media was equivalent or superior to storage in water, a comparison among storage stabilities of these disk-stored pesticides over time was necessary (Table III). The highest recoveries of benomyl, simazine, fluometuron, and atrazine occurred after 3 days of storage. Theoretically, the time zero (nonstored) samples should show the highest recovery since minimal time occurred between extraction and elution. These values may reflect the amount of variability expected between subsequent extractions on a daily basis. In this study, ±10–15% recovery variability was expected and accepted for the extraction procedure.

Longer storage periods of 90 and 180 days showed signs of pesticide loss because the percent recoveries were not only statistically different but were also outside the ±10–15% variability range (Table III). Further studies of this nature with longer storage periods are needed to confirm this inference.

Trifluralin, alachlor, methyl parathion, metolachlor, pendimethalin, norfluorazon, captan, and profenofos

Table IV. Effect of Storage Time and Storage Treatments on Percent Recovery of Stored Pesticides[a]

treatment	storage period	% recovery[d] TF	AC	MP	MC	PM	NF	CP	PF
not incubated	0	73	78	82	75	77	77	104	78
disk stored,[b] 4 °C	3	66	83	88	79	76	76	114	78
disk stored,[b] −20 °C	3	65	80	82	77	74	74	107	77
disk stored,[b] 4 °C, −20 °C	3	68	74	78	73	71	71	109	73
bottle stored,[c] 4 °C	3	67	70	74	69	69	69	28	69
disk stored, 4 °C	30	60	58	66	62	58	65	54	70
disk sored, −20 °C	30	60	60	65	60	59	65	32	69
disk stored, 4 °C, −20 °C	30	58	57	65	58	57	66	53	70
bottle stored, 4 °C	30	56	60	62	58	59	64	1	57
disk stored, 4 °C	90	73	79	86	89	79	76	32	116
disk stored, −20 °C	90	80	89	89	95	91	76	33	126
disk stored, 4 °C, −20 °C	90	82	94	100	97	86	107	46	138
bottle stored, 4 °C	90	75	82	78	80	77	87	0	84
disk stored, 4 °C	180	60	79	93	86	79	79		86
disk stored, −20 °C	180	54	75	85	77	70	70		76
disk stored, 4 °C, −20 °C	180	64	89	100	86	79	79		86
bottle stored, 4 °C	180	32	66	62	65	59	59		65
LSD (0.05)[e]		5.8	7.1	8.3	8.1	7.1	7.0	20.3	8.3

[a] Key: TF, trifluralin; AC, alachlor; MP, methyl parathion; MC, metolachlor; PM, pendimethalin; NF, norflurazon; CP, captan; PF, profenofos. [b] Pesticide/water solutions filtered and vacuum-dried through C-18 disks. [c] Pesticides stored in bottles containing 250 mL of water. [d] Mean values obtained from four determinations. [e] Least significant difference. If the difference between the two compared values is greater than the LSD, the values are considered to be statistically similar. If the difference is smaller than the LSD, the values are statistically similar.

showed a significant interaction between storage treatment and time interval (Table IV). These compounds demonstrated the trends that were discussed earlier with the previously mentioned compounds. In most cases, the disk storage of pesticides was equivalent or superior to pesticide storage in water.

Two distinct cases of statistical differences between disk storage and water storage occurred in the trifluralin and captan data (Table IV). The various storage treatments of trifluralin did not demonstrate any differences until the 180-day storage period. After 180 days of storage, trifluralin stored in bottled water gave 32% recovery while recovery from disks ranged from 54 to 64%, representing about a 50% loss of pesticide when stored in water compared with disk storage. This loss would double the sensitivity and detection limits of samples stored over this duration. Similar trends of pesticide loss were shown for alachlor, metolachlor, methyl parathion, pendimethalin, norflurazon, and profenofos; however, over the 180 days of storage in water their loss was not as great as found for trifluralin (Table IV). Captan demonstrated the most dramatic results (Table IV). The recovery from water stored for 3 days at 4 °C was 28% whereas the recovery from disks stored at 4 °C was 114%. The differences were more pronounced after 30 days, when captan had all but completely dissipated in water while 32–54% was recovered from disk storage. This stabilizing ability of the C-18 material had been observed by other researchers, who stated that materials bonded to a solid phase were more stable (*1*).

It is also apparent from these data that disk storage does not totally solve the stability problem of captan. Observation of the 30-day results for this compound indicates significant loss of the parent captan over that time span. This loss may be due to hydrolysis by water that could not be totally removed from the disk by vacuum filtration. Therefore, captan would still be in an aqueous environment and susceptible to hydrolytic attack even while it resides in the nonpolar matrix of the C-18. It may be possible to further stabilize these compounds by removing the residual water through desiccation, lyophilization, or blotting with anhydrous sodium sulfate prior to permanent storage.

When the disks were dried by pulling a vacuum on them for 5 min as stated in the precedure, freezing did not affect their pliability. No attempt was made to determine the effect of a shorter drying time. Since the frozen disk treatments gave the highest recovery with no deleterious effects upon continuing the extraction procedure, freezing the disk after extraction and temporary storage seems to be the best approach. In addition, the 90- and 180-day storage period disk treatments at 4 °C exhibited microbial growth. This may have been a factor in the slightly lower recoveries for these disk-stored treatments. Microbial growth was not observed on the frozen disk storage treatments, therefore supporting the advantage to freezing the disk after loading the pesticides.

Summary

The stability of these pesticides has been preserved and in most cases enhanced by concentrating the pesticides on C-18 material. Trends appear to favor storage of pesticides on the disk by freezing after extraction onto the C-18 material. These results offer promising possibilities that could alter the way water samples containing these pesticides are currently stored. The pesticides were both stabilized and extracted by the nonpolar media of the disk. Therefore, water samples that formerly occupied the space necessary for 500–1000-mL bottles may be reduced to a 0.5 mm thick × 47 mm diameter pliable filter. The reduction in storage space is clearly and quickly realized. Field extraction using SPE disks appears to be the next logical step in developing and utilizing the potential of the extraction disks. Through field extraction, pesticides could be both concentrated and stabilized on a disk while in the field. The disk could then be stored rather than a bulky glass jar. While increased time would be required for sample collection, a part of the normal laboratory extraction procedure would have been performed in the field. Consequently, sample preparation time in the laboratory would be decreased, thereby allowing a quicker analysis. In addition, transport of pesticide samples through the mail from one laboratory to another may be easier and cheaper if disks are used as the storage containers rather than bottles. Drawbacks of this type of storage scheme, such as that found with captan, must be studied more completely. Further studies need to explore more complete removal of water from the disks as a means of stabilizing the bound pesticides. A continuing data base should also be constructed for the stability of other organic compounds on SPE disks. The completion of these tasks would accelerate the development of SPE techniques in laboratories and would lessen the severity of problems often encountered by these establishments.

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