

## ARTICLES

## Recovery of Synthetic Pyrethroids in Water Samples during Storage and Extraction

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Monitoring for synthetic pyrethroids in surface water at the sub-parts per billion level requires reproducible sampling and analytical methods. We studied the recovery of bifenthrin, permethrin, and deltamethrin in water during storage in glass containers and extraction using solid-phase membranes. In solid-free water, the concentration of all compounds quickly decreased and then remained constant at 58–72% of the initial concentration, likely due to adsorption to the glass surface. The recovery was enhanced in runoff samples that contained suspended solids, which was attributed to the association of pesticides to the suspended solids. However, the greatest loss occurred when runoff samples were not agitated before extraction, and the loss was largely caused by the exclusion of the suspended solids from the aqueous phase. Nearly 100% extraction recoveries were obtained when C<sub>8</sub> or C<sub>18</sub> membranes were used for extracting runoff samples. Adsorption to glass surfaces and suspended solids can result in substantial underestimation of pyrethroid concentrations or biological activity and therefore should be considered when designing monitoring protocols.

**KEYWORDS:** bifenthrin; permethrin; deltamethrin; synthetic pyrethroids; adsorption; storage stability; artifacts

Synthetic pyrethroid insecticides are widely used for controlling many agricultural and urban pests. The use of synthetic pyrethroid insecticides is expected to increase further as several organophosphate insecticides, including diazinon and chlorpyrifos, are being phased out for certain uses. Although known for being highly immobile in soil, synthetic pyrethroids can enter surface water via runoff after adsorption to soil or sediment particles (1–3). Most synthetic pyrethroids possess apparent toxicity to fish and other aquatic organisms, including aquatic invertebrates, often at concentrations less than 1  $\mu\text{g L}^{-1}$  (1, 4, 5). Therefore, monitoring for pyrethroid insecticides in urban and rural surface streams will be important, and reliable sampling and analytical procedures are urgently needed.

Sampling of surface water is commonly carried out using glass bottles as sample containers during sample collection, transportation, and storage. However, previous studies showed that permethrin was substantially adsorbed from water onto glass and several plastic surfaces (6). Low recoveries after storage in glass containers were also reported for esfenvalerate (7) and  $\lambda$ -cyhalothrin (8). Furthermore, surface water typically contains

suspended soil or sediment particulates. It is known that synthetic pyrethroids have high affinity to such soil or sediment materials (1, 9, 10). It is therefore suspected that adsorption to suspended solids could also contribute to the low recoveries (7, 8). However, both loss pathways may occur during sample collection and storage, and simultaneous evaluation is needed for a better understanding of sample stability in glass containers.

The potential loss of pyrethroids due to adsorption to glass surfaces or solids also implies that rapid extraction methods are needed to minimize sampling-derived errors. The analytical method currently used for monitoring involves the extraction of whole samples (without removal of suspended solids) with ethyl acetate (11). This method consumes relatively large quantities of solvents and is also labor intensive because of multiple extractions and concentration of extracts. Solid-phase extraction using C<sub>8</sub> or C<sub>18</sub> columns has been reported for recovering pyrethroids from water samples (7, 12–14). Compared to columns, solid-phase membranes allow rapid passing of large volume of samples, further shortening the time needed for extraction. However, the efficiency of solid-phase membranes for extracting pyrethroids from surface water has not been evaluated. The objectives of this study were to characterize adsorption loss of pyrethroid compounds to glass during sample collection and storage, to characterize the role of suspended

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solids in recovery, and to evaluate the performance of C<sub>8</sub> and C<sub>18</sub> membranes in extracting these pesticides from surface water.

## MATERIALS AND METHODS

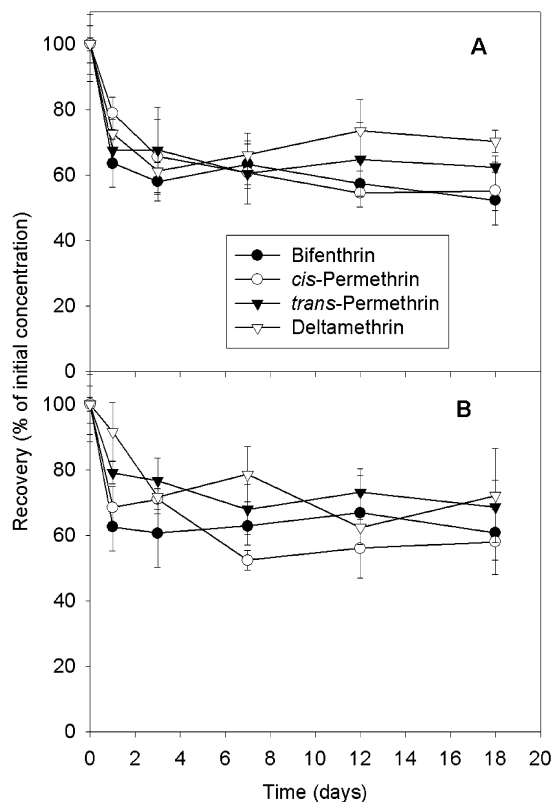
**Chemicals and Glass Containers.** Three pyrethroid insecticides, bifenthrin, permethrin, and deltamethrin, were selected for this study. Standards of bifenthrin (>98% purity), permethrin (20% *cis* isomer and 78% *trans* isomer) and deltamethrin (>99% purity) were purchased from Chem Service (West Chester, PA). Organic solvents used in extraction were all of pesticide or HPLC grade. The sample containers used for the storage stability evaluation were I-Chem 1.0 L flint glass bottles that were amber-colored and precleaned to meet EPA requirements (Fisher Scientific, Pittsburgh, PA). The screw caps were made of polypropylene and were fitted with Teflon fluorocarbon resin liners.

**Storage Stability Experiments.** To determine the stability of synthetic pyrethroids in water during storage in glass containers, deionized (DI) water and runoff samples were spiked with bifenthrin, permethrin, and deltamethrin, and pesticide recovery was followed up to 18 days. The runoff water was collected from a drainage channel at a commercial nursery site located in Orange County, CA. The runoff water contained suspended solids at 25.4 mg L<sup>-1</sup>, as determined by filtration through 0.5 μm glass fiber membranes before use. The pH was measured to be 7.01. A 500 mL aliquot of DI or runoff water were transferred to the sampling bottles by weighing to 0.1 g. Each sample bottle was then spiked with 2.0 μL of acetone solution containing each pyrethroid at 0.5 mg mL<sup>-1</sup>. The initial concentration of each pyrethroid in the water samples was therefore 2 μg L<sup>-1</sup>. The treated samples were then capped and equilibrated in a refrigerator at 4 ± 0.5 °C or an incubator at 20 ± 0.5 °C.

Triplicate samples were removed from the storage on day 0, 1, 3, 7, 12, and 18 after treatment and were extracted and analyzed. For DI water samples, the sample was agitated by vigorously shaking the bottle and the content was emptied into a 1 L glass separatory funnel. A 100 mL aliquot of ethyl acetate was added into the funnel and the mixture was vigorously shaken for 1 min. The ethyl acetate fraction was collected upon phase separation. The same phase partitioning process was repeated for a total of three consecutive times. The ethyl acetate extract was combined and 30 g of anhydrous sodium sulfate was added to remove water. The ethyl acetate extract was then concentrated on a rotary evaporator at 60 °C to near dryness, and a hexane-acetone (1:1, v/v) mixture was used to rinse the flask and to bring the final volume to 5.0 mL. An aliquot of the final extract was transferred to an autosampler vial for analysis on gas chromatography (GC). Preliminary experiments showed that the recovery of bifenthrin, permethrin, and deltamethrin after ethyl acetate extraction was close to 100%.

For the runoff water samples, two different methods were used to handle the samples prior to extraction. One set of samples were subjected to vigorous shaking to resuspend the settled solid particles, and the content was immediately transferred to the separatory funnel. This treatment allowed both the aqueous and solid phases to be included for extraction. Another set of samples were transferred without agitation. This treatment caused exclusion of the settled solids from extraction. The same procedures as described for DI water samples were used for the extraction of runoff samples. The extracts were concentrated and redissolved in hexane-acetone (1:1, v/v) for GC analysis. To determine the fraction of pesticides that was associated with the settled solids and therefore was excluded from the aqueous phase, sample bottles were rinsed with 50 mL hexane-acetone (1:1, v/v) for three times. The extracts were combined and concentrated to 5.0 mL for GC analysis.

**Evaluation of Solid-Phase Extraction Methods.** Samples made of DI water or runoff water were spiked with solution of bifenthrin, permethrin, and deltamethrin to arrive at an initial concentration of 2 μg L<sup>-1</sup> for each pesticide. These samples were kept at the ambient temperature for less than 2 h before they were extracted using the following methods. Samples were passed through a 5 cm C<sub>8</sub> or C<sub>18</sub> extraction membrane (3M, St. Paul, MN) under vacuum. The upper layer (containing less solids) of the aqueous solution was transferred first and the lower layer (containing more solids) was added later to prevent clogging. The sample container was rinsed with 50 mL of DI water, and the rinse solution was also passed through the membrane.



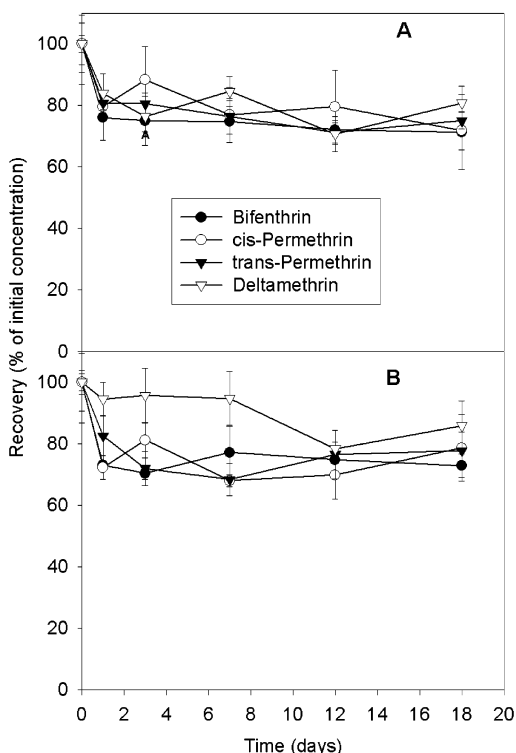
**Figure 1.** Recovery of bifenthrin and permethrin during storage of fortified deionized water samples in glass bottles: (A) 4 and (B) 20 °C.

To determine the recovery of pesticides on the solid-phase membrane, the membrane was placed in a 20 mL glass vial containing 5.0 mL of hexane-acetone (1:1, v/v) and the sample was sonicated for 15 min in a 130 W and 50–60 Hz sonicator (Fisher). An aliquot of the extract was transferred to an autosampler vial for GC analysis. Preliminary experiments showed that this extraction procedure resulted in nearly 100% recovery of the pyrethroid compounds from the SPE membranes. The fraction of pesticides that passed through the membrane was quantified by extracting the filtrate with ethyl acetate using the same procedures as given above for recovering pesticides from aqueous samples.

**GC Analysis.** An Agilent 6890N GC system (Agilent Technologies, Wilmington, DE) was used for the detection and quantification of bifenthrin, permethrin isomers, and deltamethrin in sample extracts. The GC system was equipped with a micro-electron capture detector (ECD). A capillary column (Agilent-5, 30 m × 0.32 mm × 0.25 μm) was used with helium as the carrier gas at 2.1 mL min<sup>-1</sup>. The other GC parameters were as follows: inlet temperature, 250 °C; detector temperature, 300 °C; oven temperature, initially 150 °C for 1.0 min, ramped to 280 °C at 15 °C min<sup>-1</sup>, and kept at 280 °C for 5.0 min; and injection volume, 1.0 μL. Samples were introduced in the splitless mode. Under these conditions, the retention time for bifenthrin, *cis*-permethrin, *trans*-permethrin, and deltamethrin was 9.0, 10.2, 10.3, and 11.1 min, respectively.

## RESULTS AND DISCUSSION

**Storage Stability of Solid-Free Water.** Recovery of bifenthrin, permethrin, and deltamethrin from DI water during storage in glass bottles is shown in Figure 1. At either 4 or 20 °C, there was a substantial decrease in pesticide concentration, and the decrease was most noticeable within the first 3 days of storage, with the greatest decrease occurring within the first 24 h. Pesticide concentration in the aqueous phase varied relatively little between day 3 and day 18. If the averaged pesticide concentrations from day 3 to day 18 were used for comparison, the concentration of bifenthrin, *cis*-permethrin, *trans*-permethrin,

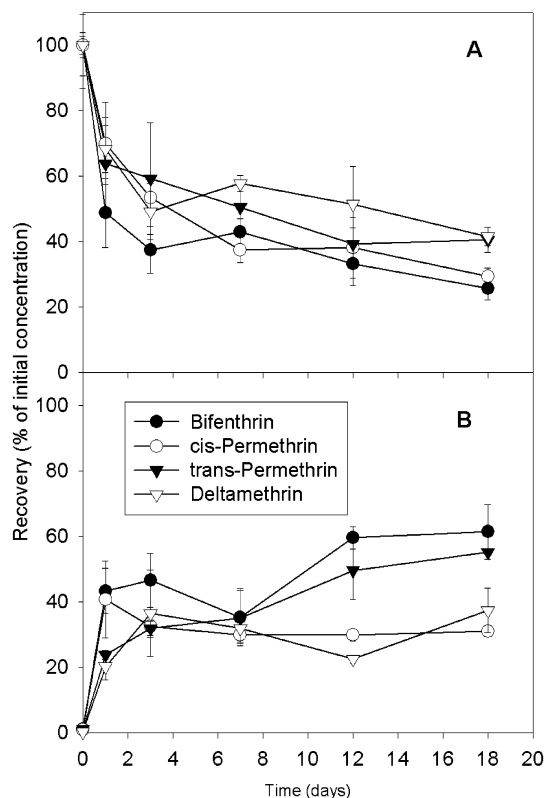


**Figure 2.** Recovery of bifenthrin and permethrin during storage of fortified runoff water in glass bottles: (A) 4 and (B) 20 °C. Samples were resuspended before extraction.

and deltamethrin decreased by 37, 29, 41, and 28%, respectively, when stored at 4 °C. On day 1, the respective reductions were 37, 28, 21, and 32%. The rapid dissipation during the initial hours suggests that samples should be analyzed immediately following sampling to avoid loss of recovery. The fact that DI water was used and that samples were incubated in amber-colored bottles in the dark also suggests that the loss of pyrethroids during storage was likely caused by adsorption to the inside glass surface of the sample container. Adsorption of permethrin to glass surfaces was first reported by Sharom and Solomon (6) in scintillation vials that were made of borosilicate glass. Adsorption loss increased rapidly for the first 24 h of contact and did not change from 48 to 120 h. The same researchers also observed that adsorption loss of permethrin was dependent on the ratio of surface area of contact to sample volume; as the ratio was increased from 2.1 to 3.1 cm<sup>2</sup> mL<sup>-1</sup>, the loss of permethrin after 5 days of storage increased from 42 to 70%. The ratio of surface area to sample volume in this study was measured to be 1.6 cm<sup>2</sup> mL<sup>-1</sup>. The loss of total permethrin at 20 °C in this study was 36%, which compared well with the 42–70% range observed by Sharom and Solomon (6). When the pair-*t* test was used to compare pesticide concentrations remaining in the container from day 3 to day 18, no significant difference was found between the different pesticides under the same temperature. Similar statistical analysis was also used to compare the different temperature treatments for the same pesticides. Only the recovery of *trans*-permethrin was significantly ( $P = 0.001$ ) lower at 20 °C than at 4 °C. Therefore, for solid-free water samples, similar magnitudes of losses may occur to different pyrethroids during their storage in glass bottles, and the loss may be generally independent of temperature between 4 (refrigerator) and 20 °C (typical room temperature).

#### Storage Stability of Water Containing Suspended Solids.

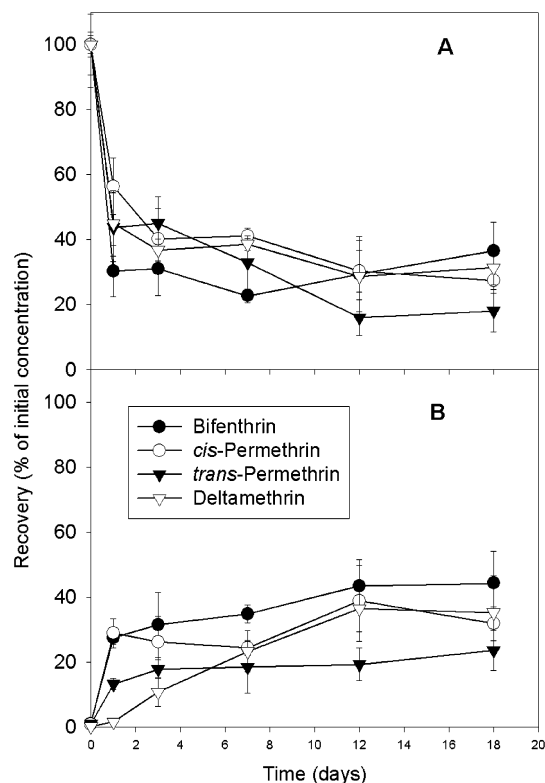
Surface water commonly differs from DI water in that the former



**Figure 3.** Recovery of bifenthrin and permethrin during storage of fortified runoff water in glass bottles at 4 °C: (A) recovery from aqueous phase and (B) recovery from settled solids. Samples were not resuspended before extraction.

contains certain amounts of suspended solids. Some of the suspended solids will gradually settle out of the aqueous phase during storage. To understand the effect of suspended solids, the runoff samples were processed with or without agitation before extraction to include or exclude the separated solids. When the samples were agitated to resuspend the settled particulates, the recovery generally decreased for all of the pyrethroid compounds within the first 3 days of storage and remained unchanged thereafter (Figure 2). No significant difference was found for the different pesticides under the same storage temperatures. The overall reduction in recovery ranged from 21 to 30% at 4 °C and from 12 to 26% at 20 °C. The effect of temperature was also insignificant for the same pesticides. However, when compared with the DI water samples, recovery of pesticides from the runoff samples was generally higher. For instance, at 20 °C, significantly more bifenthrin ( $P = 0.003$ ), *cis*-permethrin ( $P = 0.02$ ), *trans*-permethrin ( $P = 0.05$ ), and deltamethrin ( $P = 0.0008$ ) were recovered from the runoff samples than from the DI water samples (Figures 1b and 2b).

When the runoff samples were not agitated, much greater losses of recovery were consistently observed at either 4 or 20 °C (Figures 3 and 4). It also appears that the concentration decrease was the greatest within the first 3 days and became more gradual thereafter. At 4 °C, only 26, 29, 40, and 41% of the original pesticide was recovered on day 18 for bifenthrin, *cis*-permethrin, *trans*-permethrin, and deltamethrin, respectively. At 20 °C, the respective recoveries on day 18 were only 36, 27, 18, and 31% (Figure 4a). Because of the lack of agitation, it was visible that solids were separated from the aqueous phase and became attached to the glass surface inside the sample container. Analysis for pesticides in the solid phase showed that



**Figure 4.** Recovery of bifenthrin and permethrin during storage of fortified runoff water in glass bottles at 20 °C: (A) recovery from aqueous phase and (B) recovery from settled solids. Samples were not resuspended before extraction.

**Table 1.** Physicochemical Properties of Synthetic Pyrethroids Used in the Study

parameter	bifenthrin	permethrin	deltamethrin
molecular weight	423	391	505
solubility (mg/L, 20 °C)	0.1	0.2	0.002
vapor pressure (mPa, 25 °C)	0.024	0.0013	0.002
$K_{ow}$ (20 °C)	1 000 000	1 260 000	270 000
$K_{oc}$ (mL g <sup>-1</sup> ) (16)	240 000	100 000	186 000

concurrent to the decreasing concentrations in the aqueous phase, the fraction of pesticides associated with the settled solids increased with time, at both 4 and 20 °C (Figures 3b and 4b). For instance, at 4 °C, as much as 31–61% of the added pesticides were found with the soil particles at the end of the 18 day equilibration period (Figure 3b). The greatest increase in the solid-phase concentration occurred at the beginning of sample storage, which coincided with the greatest decrease in the aqueous-phase concentration. These results clearly indicate that, in water samples that contain suspended solids, pyrethroids are adsorbed to the solids and that when the solids settle out from the aqueous phase, an extraction method without inclusion of the solids will give low pesticide recoveries. It is also important to note that adsorption to suspended solids may also cause underestimation of toxicity to aquatic organisms in toxicity evaluation and identification assays. The strong adsorption of bifenthrin, permethrin, and deltamethrin can be inferred from their  $K_{ow}$  and  $K_{oc}$  values (Table 1) (15) and is typical also for other synthetic pyrethroid compounds (1, 16). It can be further concluded that the effect of suspended solids on the recovery of pyrethroids will directly depend on the level and maybe type of suspended solids in the water. This artifact, however, can be

**Table 2.** Recovery of Synthetic Pyrethroids in Different Fractions during Solid Phase Extraction of Fortified Water Samples

fraction	distribution (%)		
	bifenthrin	<i>cis</i> -permethrin	<i>trans</i> -permethrin
Fortified Deionized Water			
C <sub>8</sub> disk	87.2 ± 1.0	82.9 ± 0.3	83.8 ± 3.7
filtrate	12.8 ± 1.0	17.1 ± 0.3	16.1 ± 3.6
C <sub>18</sub> disk	97.0 ± 5.2	95.0 ± 4.1	93.7 ± 2.8
filtrate	3.0 ± 0.6	5.0 ± 0.7	6.3 ± 0.4
Fortified Runoff Water			
C <sub>8</sub> disk	99.2 ± 0.8	98.5 ± 0.2	99.1 ± 0.1
filtrate	0.8 ± 0.1	1.5 ± 0.2	0.9 ± 0
C <sub>18</sub> disk	99.6 ± 0.1	99.3 ± 0.1	99.6 ± 0.2
filtrate	0.4 ± 0	0.7 ± 0	0.4 ± 0

prevented if thorough agitation is performed to the sample prior to extraction or if extraction is made immediately after sampling.

**Recovery of Solid-Phase Extraction.** Recovery of bifenthrin, permethrin, and deltamethrin was determined by solid-phase extraction using C<sub>8</sub> or C<sub>18</sub> membranes. For the DI water samples, 83–87% of the spiked pesticides was recovered on the C<sub>8</sub> membrane and 94–97% was recovered on the C<sub>18</sub> membrane (Table 2). The recovery with C<sub>18</sub> membranes was significantly ( $P < 0.01$ ) better than that with C<sub>8</sub> membranes. However, it is also clear that when the SPE membranes were used for extracting solid-free water samples, a small fraction of the pyrethroids did break through the adsorbent and was not recovered. Recovery of all compounds was substantially improved when the same method was applied to runoff samples that contained a significant amount of suspended solids (Table 2). The averaged recoveries were close to 100% for both C<sub>8</sub> and C<sub>18</sub> membranes. The enhanced recovery may be attributed to the fact that a large fraction of pesticides in the runoff samples were associated with suspended solids that became retained by the SPE membranes during extraction.

Compared to traditional extraction techniques such as solvent–solvent partitioning, solid-phase extraction uses only a marginal amount of organic solvents. Previous studies showed that synthetic pyrethroids in aqueous samples could be quantitatively recovered using columns packed with the C<sub>8</sub> or C<sub>18</sub> adsorbent (12–14). Our study indicates that good recoveries could also be obtained by passing samples through C<sub>8</sub> or C<sub>18</sub> membranes. Although operating on the same mechanisms, C<sub>8</sub> or C<sub>18</sub> membranes allow larger volumes of aqueous samples to pass through the adsorbent in a shorter time, thus further accelerating sample preparation. However, it was observed that passing agitated runoff samples resulted in immediate clogging of the membranes. The speed of filtration was greatly improved when the samples were allowed to settle prior to the extraction and the clear portion was transferred first. Complete filtration was obtained usually within 10 min for 250 mL samples.

In conclusion, trace analysis of organic contaminants such as synthetic pyrethroids in surface water must be scrutinized due to the high affinity of such compounds to environmental substrates and even sampling devices. Our study showed that simultaneous adsorption to glass surface and suspended solids during sampling and sample storage may result in detection of synthetic pyrethroids at artificially low concentrations. To eliminate or reduce such artifacts, it is important to perform extraction shortly after samples are collected and to take measures to include the suspended solids in extraction. Using solid phase membranes essentially eliminates the use of solvent and may also add to speedy sample preparation.

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