J. of the Environmental Sciences
Vol. 12, No. 8, 891~896, 2003

Distribution of Pyrethroid Insecticides in a Nursery Drainage Channel

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(Manuscript received 7 July, 2003; accepted 23 August, 2003)

The objectives of this study were to investigate the effect of two synthetic pyrethroids, bifenthrin(BF) and permethrin(PM), in runoff and to evaluate the effect of suspended solids (SS) in the transport of pyrethroid along the drainage channel. Monitoring of BF and PM was conducted with the runoffs as well as in sediments existing along the drainage channel at a nursery site located in southern California, USA. This study also suggests Best Management Practices (BMPs) to alleviate the pollution caused by heavy usage of pyrethroid insecticides at nursery sites. Due to a high affinity to solid particles of pyrethroid insecticides, the concentrations of BF and PM were proportional to the SS contents along the drainage channel. This study suggests that alleviation of pyrethroids existing in runoffs could be controlled by the removal of suspended solids in runoffs and potential implications of current drainage channels for mitigation of pesticides associated with runoffs.

Key Words : Pyrethroids, BMPs, Bifenthrin, Permethrin, Runoff

1. Introduction

Nursery production plays critical roles in southern California, USA. However, the heavy use of pyrethroid insecticides causes significant effects on aquatic organisms and draws into the destruction of aquatic ecosystems in near coastal areas.

Synthetic pyrethroid insecticides are used heavily for controlling pests in agricultural and urban areas.[1] Commercial nurseries are widely using pesticides and fertilizers. These uses, when coupled with intensive overhead sprinkler and drip irrigation, often result in substantial water runoff at nursery sites. Many pesticides used in nurseries are organophosphate and synthetic pyrethroid insecticides, chemicals that have high toxicities towards fish and other aquatic organisms.[1] The presence of these pesticides in urban streams has the potential to cause an adverse impact on aquatic ecosystem. However, it is poorly understood how these contaminants are entering runoffs and mitigation options are few.

Bifenthrin and permethrin have been chosen for this study as target pesticides because they are commonly used at nursery sites. These synthetic pyrethroids are considered replacements to some organophosphate insecticides. Synthetic pyrethroids have generally little or no mammalian toxicity, but are potent to many pests when applied at even very low rates. However, most pyrethroids have extremely high toxicities towards fish and aquatic invertebrates.[2,3] Pyrethroid insecticides are essentially immobile in the environment due to their strong adsorption in soil.[1] Therefore, a unique mechanism must have been in operation that caused pyrethroid runoff from nursery operations.

Soil and sediment play a critical role as environmental sinks to alleviate the impact of pollution issues. The behavior of the pesticides has been invoked and extensively studied by many investigators in both the laboratory and the field. However, little is known about the

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fate of pyrethroids in sediment resulting from nursery runoff. Continuous runoff results in the buildup of organic matter-rich sediment in the path of the runoff, and the sediment is often left in the channel for a long time before clean-up. Thus the sediment over which the runoff flows serves as a reservoir for prolonged release of bifenthrin and permethrin. The persistence of bifenthrin and permethrin in sediment, and their partitions between water and sediment, can determine how far these pesticides can travel downstream, and how long they can potentially affect the impacted water bodies.

The sorbed chemical transport in overland flow has been studied by various researchers using an enrichment ratio (ER) for the prediction of chemical transport.[4,5] It was also elucidated that the effect of raindrops did not lead to the total collapse of soil aggregates, and stripping by raindrops could be the major cause of chemical enrichment in the eroded sediment. The effect of rain events in herbicide transport in drainage was investigated.[6] However, no studies have been investigated to find out the effect of solid materials for the transport of pyrethroids in nursery drainage channels.

The objectives of this study were to characterize nursery runoffs by examining suspended solids and to evaluate the potential effect of suspended solids and sediment in the transport of pyrethroids along the channel. Some information from this study can also be used for designing Best Management Practices (BMPs) to alleviate adverse effects from the use of pyrethroid compounds and for utilizing current drainage channels for the mitigation of pesticides associated with runoffs.

2. Materials and Methods

2.1. Chemicals

Two pyrethroids, bifenthrin and permethrin, were selected for this study. Standards of bifenthrin (>98% purity) and permethrin (20% cis isomer and 78% trans isomer) were purchased from Chem Service (West Chester, PA, USA). Ethyl acetate, hexane and acetone (99% purity, pesticide grade) were purchased from Fisher Scientific (Pittsburgh, PA, USA) and used as solvents for liquid as well as solid phase extraction.

2.2. Drainage Channel Description and Sampling

A 260 m portion of a nursery drainage channel located in Southern California USA was chosen for this study. The runoff drains through an artificial channel and eventually into the San Diego Creek. At the nursery site, many small streams generated in various production areas converge into two main runoff paths and flow into a settling pond. Then the runoff flows along a cement-lined channel. The drainage channel was approximately 2 m wide (top width) and 1.2 m deep. The channel water width was variable depending on irrigation activity at the nursery sites. A diagram of the drainage channel used in this study is illustrated (Fig. 1)

The arrangement of best management practices (BMPs) to remove sediment and sediment-adsorbed pesticides was also made and is shown schematically in Fig. 1. The BMPs include polyacrylamide (PAM) delivery into the runoff stream, installation of an in-line sediment trap and a sediment settling pond, and a vegetative strip in the discharge channel. PAM has been used as a flocculent to cause aggregation and to help settle down suspended solids from water. The introduction of PAM before the sediment trap allows the polymer to be fully mixed in the runoff flow and allows the interaction to occur over a relatively long distance downstream.

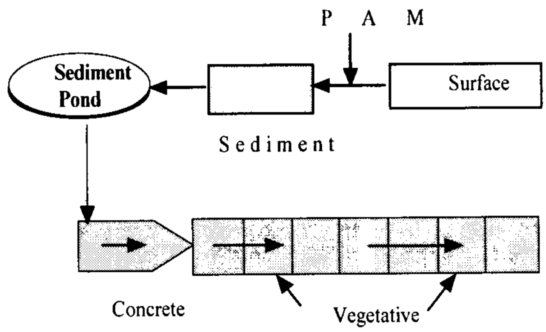

Fig. 1. Diagram of nursery drainage channel in study sites.

The sediment trap and settling pond slow down the runoff flow, allowing some of the suspended solids to settle out under gravity. In the discharge channel, several small basins were constructed with sand bags. These basins are expected to further slow the runoff flow. When significant sediment accumulation occurs in the sediment trap or pond, the sediment is mechanically cleared.

The vegetative strip contained canna lilies grown in wire baskets anchored in water. This plant helps to further slow down the flow so as to cause the settling and physical trapping of suspended solids. The canna lily strip occupies about 160m of the discharge channel.

To understand the transport and fate of pyrethroid insecticides, several sampling points within the channel were established along the vegetative strip. The runoff waters containing suspended solids were collected along with sediments that settled on the bottom of the channel. Sampling sites were assigned as follows: PAM1 (before PAM delivery), PAM2 (after PAM delivery), Pond1 (influents entering sediment pond), Pond2 (effluents leaving sediment pond), 104, 145, 166, 187, 210, 240m (distances from pond2) and OUT where the sampling site is outside of nursery property. The runoff samples were collected from the top layer of water in flow. The sample containers used for storage were I-Chem 1.0L flint glass bottles that were amber-colored and pre-cleaned to meet EPA requirements (Fisher Scientific, Pittsburgh, PA). The screw caps were made of polypropylene. However, sediment samples were stored in plastic bag. The samples were stored in storage iceboxes and transported to the laboratory for further experiments.

2.3. Evaluation of Runoff and Sediments

To evaluate the effectiveness of the various BMPs, the runoff samples have been collected at different locations along the runoff path as described in the previous section. The first sampling points were immediately before (PAM1) and after the PAM (PAM2) release points and the last sampling point was outside of the nursery property (OUT). The rest of the sampling points were demonstrated as arabic numerals in accordance with the distance along the drainage channel.

The analysis for runoff samples were conducted within 4 hours because of possible adsorption of pyrethroids into the sampling bottles made of glass walls.[7] To determine the suspended solids in runoff samples, filtration through 0.45 um glass fiber membranes was conducted. The amounts of suspended solids at each sampling site were measured (Fig. 2). The filtrates after filtration were collected and extracted by using hexane-acetone (1:1, v/v) after a drying process of 24 hours in an oven at 100°C. Filters containing suspended solids were weighed for measurements and then transferred into 20mL capacity headspace glass vials. 5 mL of hexane-acetone (1:1, v/v) was added in each vial and then sonicated for 15minutes in a 130W and 50-60 Hz sonicator (Fisher Scientific, Pittsburgh, PA, USA) to extract bifenthrin and permethrin sorbed in suspended solid fractions. An aliquot of the extract was transferred to an autosampler vial for GC analysis. The fraction of pesticides that passed through the filter was quantified by extracting the filtrate with 50mL of ethyl acetate three times for bifenthrin and permethrin existing in aqueous phase. The extracts were combined and concentrated to 5.0mL for GC analysis by following the same procedure as demonstrated in an earlier study.[7]

For the sediment phase, the samples were air dried and passed through a 2-mm sieve after using a mortar and pestle to break up clots. Obvious vegetable matter, such as wood fragments and leaf debris, were removed. Soil analyses were conducted by following the standard me-

Table 1. Physico-chemical analysis for soil used in this study

Distance	Texture Analysis			OC (%)	pH	CEC (meq/100g)
	Sand(%)	Silt(%)	Clay(%)			
Pond	35	50	15	3.36	7.7	29.1
104m*	51	39	9	5.02	8.9	36.8
166m	31	52	17	4.87	7.7	32.3
187m	36	49	15	3.93	7.6	30.7
210m	25	56	19	4.78	7.5	33.3

Note: *, distance was calculated from the origination where runoff left from sediment pond.

thods in the DANR (Division of Agricultural and Natural Resources) analytical laboratory at the University of California, Davis, and the results are presented in Table 1. To determine pyrethroid insecticides sorbed in sediments, 5 g (dry wt.) of sediments were transferred into 40mL capacity centrifuge tubes made of Teflon. 30mL of hexane-acetone (1:1, v/v) was added and then put on a platform shaker at high speed for an hour. This extraction procedure was repeated three times. The extracts were combined in a 100mL volumetric flask and filled up to 100mL with hexane-acetone (1:1, v/v). An aliquot of the extract was transferred to an autosampler vial for GC analysis.

2.4. GC Analysis

An agilent 6890N GC system equipped with an electron capture detector (ECD) (Agilent Technologies, Wilmington, DE) was used for the detection and quantification of BF and PM. An Agilent-5 capillary column (30 m x 0.32 mm x 0.25 m) was used with helium as the carrier gas at 2.1 mL min^{-1}. 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^{-1}, and kept at 280 °C for 5.0 min; and injection volume, 1.0 uL. Samples were introduced in the splitless mode. The identification of pyrethroids was carried out via comparison of retention times of peaks in the sample relative to the standard

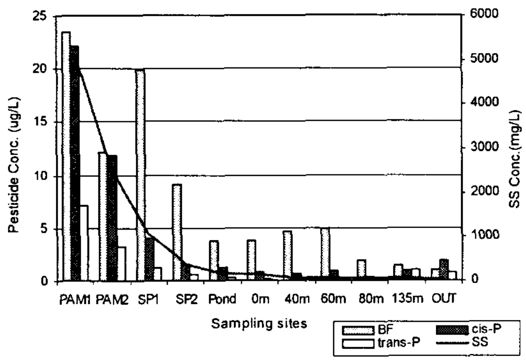

Fig. 2. Pyrethroid insecticides distribution in run-Off samples containing aqueous and suspended solid fractions. BF, bifenthrin; *cis*-P, *cis*-permethrin; *trans*-P, *trans*-permethrin; SS, suspended solids.

with the relative retention times of reference chemicals. Under these conditions, the retention time for bifenthrin, *cis*-permethrin, and *trans*-permethrin were 9.0, 10.2, and 10.3min, respectively.

3. Results and Discussion

3.1. Suspended Solid Contents in Runoff

It was observed that the initial runoff contained high levels of solids. Fig. 2 shows the decrease of suspended solid content in runoff along the runoff path. The suspended solid contents were more than 5000 mg/L at PAM1, which was before PAM release, and sharply decreased to 2500 mg/L at PAM2, which was after PAM release. Such decrease can be explained by the removal of suspended solids with an aid of PAM which flocculate to agglomerate with solid particles. The suspended solid contents gradually decreased as the distance of the channel went farther. When the PAM delivery point is used as an origin, the suspended solid removal after the sediment trap was more than 90%. More reduction occurred in the vegetative channel when the runoff reached the end of the vegetative strip by showing more than 99.5% of suspended solid removal percentages. However, it could be shown that the level of solids in the nursery runoff varied with time and on-site activity.[1)]

The removal of suspended solid contents along the channel could be explained by processes such as particle size, density, the flow rate, and water column. Under the gravitational force, large and high-density particles tend to settle down more rapidly and closer to the point of origination of PAM release.

3.2. Pyrethroids in Runoff

As shown in Fig. 2, the total concentrations in runoff counting on the concentrations of aqueous and suspended solid fractions were in proportional to the suspended solid contents along the drainage channels for both pyrethroid insecticides. The suspended solid concentrations were more than 20 g/L in PAM1, and decreased sharply into less than 2 g/L at the last sampling point located outside of the property. However, the pattern described by the distribution of suspended solids along the channel was somewhat

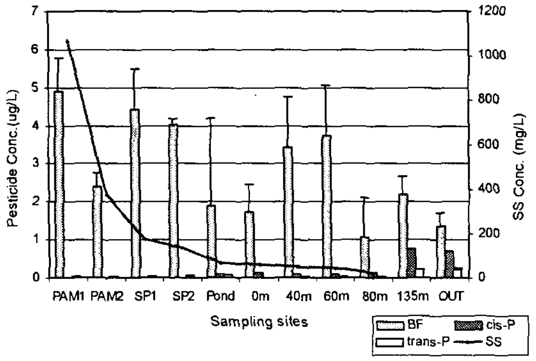

Fig. 3. Pyrethroid distribution in aqueous phase and suspended solid concentrations in runoff samples.

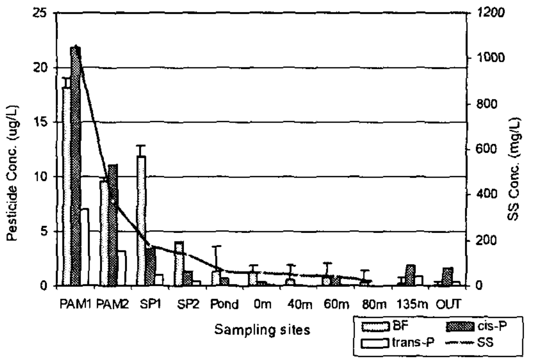

Fig. 4. Pyrethroid distribution along with suspended solid concentrations in runoff samples.

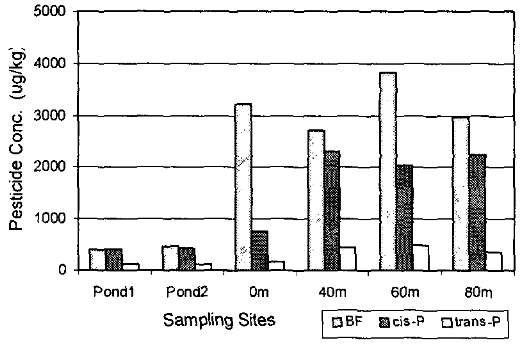

Fig. 5. Pyrethroid distribution in sediment phase.

different with that of the pesticide concentrations when the aqueous samples were combined for analysis (Fig. 3). Fig. 2 demonstrates the relationship between suspended solid concentrations and pesticide concentrations in the runoff containing both aqueous as well as suspended solid phases. Meanwhile, Fig. 3 showed the concentrations of pesticide in aqueous phase only. Not containing us suspended solid concentrations along the channel. These findings drove us to the conclusion that no distinctive relationship between concentrations in aqueous fraction and suspended solid contents was observed. However, it was evident that pyrethroid concentrations in suspended solid fractions were well matched with the pattern of suspended solid contents along the drainage channels (Fig. 4). It is explained that the pyrethroid concentrations were proportional to the levels of suspended solids. This phenomenon might be explained by the fact of extremely high sorption affinity into solid materials.[8,9]

3.3. Pyrethroids in Sediment

The measurements of pyrethroids were conducted along the channels, except for PAM1 and PAM2 and outside of the property because of the unavailability of sampling. Measurements of bifenthrin and permethrin along the 260-m channel showed dramatic bifenthrin and permethrin enrichment in the sediment. Average concentrations were 300-3800 for bifenthrin, 300-2400 for cis-permethrin, and 100-700 ug/kg for trans-permethrin (Fig. 5). It was a general trend as the pyrethroid concentrations also increased as the channel distance increased.[8] This may be attributed to the fact that the settling of suspended solids over distance is a particle size discretion process. Most large particles settled out at the site close to the origination where PAM was released. This can be explained by the fact that large particles tend to have smaller specific surface areas and lower organic matter or clay content than small particles. Therefore, the concentration of enriched pyrethroids in sediment was the highest at the farthest points downstream (Fig. 5).

4. Conclusions

Uncontrolled runoff at commercial nurseries can result in pesticide and nutrient contamination of urban streams. The use of BMPs to pesticide load at the nursery site was effective in decreasing suspended solid fractions in the runoff. Overall, the removal of suspended solids by these BMPs approached 97-99%, with significant reduction of pyrethroid concentrations showing more than 90%. Our study suggests that the removal of suspended solid fractions in the runoff was necessary to decrease pyrethroid concentrations at nursery sites. However, the persistence of bifenthrin and permethrin in sediment and its partitioning between water and sediment will need to be investigated further in the near future.

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