Pyrethroid insecticides in nursery runoff: Transport and impact on aquatic invertebrates

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Abstract

The research focus of this project is to evaluate behavior and ecotoxicological effects of synthetic pyrethroids in runoff on aquatic organisms. Synthetic pyrethroids are widely used insecticides in both urban and agricultural environments. The use of pyrethroids is likely to increase further as the use of some popular organophosphates is being restricted. Pyrethroids display high toxicity to a wide range of aquatic organisms including invertebrates, but also strong affinity to sediment and soil particles. In runoff or stream effluents, pyrethroids are expected to partition between the solid phases and the dissolved phase. Because only the dissolved chemical concentration is considered bioavailable, the actual toxicity of pyrethroids may be regulated by the level and properties of the suspended solids and dissolved organic matter (DOM) in runoff. However, current water quality programs require that the whole effluent is extracted and the total chemical concentration is determined. Such practices will likely result in erroneous estimation of toxicity.

With the support of this grant, we developed a solid phase microextraction (SPME) method that offers selective detection of the dissolved concentration. We further evaluated the application of this method for biomimetic sampling. This method has been used to study phase distribution of a number of pyrethroids in water systems containing suspended solids. We have demonstrated that in runoff effluents containing suspended solids at 100 mg L^{-1}, a significant fraction of pyrethroids was associated with the solid phase and DOM. The freely dissolved concentration was inversely proportional to the content of suspended particulates and DOM. Using ^{14}C-labelled compounds, we further found that bioaccumulation of pyrethroids decreased with increasing levels of suspended solids. Using EPA protocols, we also showed that the acute toxicity of pyrethroids in sediment suspensions decreased with increasing levels of suspended particulates and DOM. It appears that both the amount and properties of suspended solids and DOM affect the bioavailability and toxicity of pyrethroids. The inhibitory effect of suspended solids and DOM on bioavailability and toxicity should be considered in monitoring efforts as well as establishing water quality standards for pyrethroid compounds.
During this project, we have closely collaborated with a range of stakeholders in carrying out this project. Our collaborators include nursery growers in Orange County and Ventura County, farm advisors, and regulatory agencies (e.g., SWRCB, Santa Ana RWQCB, CDPR). We have obtained extramural financial support from CDPR as well as from SWRCB.

Introduction and Problem Statement

Nursery production is a multi-million dollar industry in California. To maintain plant vigor, pesticides and fertilizers are used heavily at nursery sites, and such uses are often coupled with intensive overhead sprinkler and drip irrigation. These processes lead to phenomenal runoffs and discharge of pesticides, nutrients, and sediments in the runoff. Because many nurseries are situated in urban environments, nursery runoffs can impose direct threats to water quality of urban watersheds (e.g., creeks) and the well being of exposed residents. One of the most frequently detected pesticides is bifenthrin, a pyrethroid insecticide used for control of fire ants in potting mix. The detected concentration of bifenthrin in the runoff, even though in the lower ppb range, still greatly exceeds the LC50 values for most aquatic organisms. Detection of pyrethroid insecticides in nursery runoff is disturbing. Pyrethroid insecticides are considered as replacements to diazinon and chlorpyrifos that are undergoing phase-out. Pyrethroids are thought to be safer because they have very low mammalian toxicity and are essentially immobile in the environment due to their strong adsorption to soil. These properties are usually believed to counteract their high aquatic toxicity, making them safe for aquatic ecosystems. Therefore, a unique mechanism must have been in operation that caused pyrethroid runoff from nursery operations.

Information is urgently needed to better understand behavior and potential effects of pyrethroids in nursery runoff. First, there is a lack of knowledge for better assessing the implication of pyrethroids in nursery runoffs for water quality. The existing aquatic LC_{50} values are measured in clean water, but nursery runoff always contains suspended solids and dissolved organic matter (DOM). It is known that pyrethroids are strongly adsorbed on soil particles. For instance, the K_{oc} for bifenthrin is >100,000. Therefore, a large fraction of bifenthrin in runoff may be associated with the suspended solids and DOM. Previous studies showed that adsorption to suspended solids and DOM reduced the bioavailability of hydrophobic chemicals, rendering them less toxic to aquatic organisms. Therefore, total bifenthrin concentration (sorbed + dissolved), as reported most monitoring studies, is *not* a good indicator for aquatic toxicity. To gain a more accurate assessment, it is critical to understand the effect of level and makeup (size and organic matter content) of suspended particles and DOM on aquatic toxicity of bifenthrin in nursery runoffs.

Secondly, little is known about the fate of pyrethroids in sediment resulting from nursery runoff. Continuous runoff results in buildup of organic matter-rich sediment in the path of runoff, and the sediment is often left in the channel (or creeks) for a long time before cleaning up (if ever). Our preliminary measurement of bifenthrin in the sediment along a 150-m stream at one nursery site showed dramatic bifenthrin enrichment in the sediment, and the average concentration was 2,500-3,500 ppb (μg/kg). The concentration also increases with time as more bifenthrin is partitioned into the sediment from the overlaying runoff water. Thus, the sediment over which runoff flows serves as a reservoir for prolonged release of bifenthrin. The persistence of bifenthrin in the sediment, and its partition between water and sediment, will determine how far bifenthrin can travel downstream, and how long bifenthrin will potentially affect the impacted water bodies.

The scope of the problem is hardly limited to bifenthrin alone. Many other pyrethroid insecticides, such as permethrin, cypermethrin, esfenvalerate, and cyfluthrin are also used on outdoor containers. Nor is the problem limited to the nurseries in Orange County, as nursery production is distributed throughout California. Further, the problem is not isolated only to nurseries, as there are many other uses of pyrethroids, such as for pest control of structures, landscapes, orchards (e.g., peach), vegetables (e.g., lettuce), and farm crops (e.g., cotton). Similar contamination of water bodies can occur from spray drift as well as runoff. As diazinon and chlorpyrifos are being phased out and other OP and carbamate insecticides are undergoing scrutiny, the use of pyrethroids is projected to increase significantly in the future. This study may provide crucial information that can be used to predict the potential impact of pyrethroids on affected water bodies. 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 developing TMDLs for water bodies that may be impaired with pyrethroids and sediment.

Objectives

The overall objective of this project is to evaluate the potential impact of pyrethroid insecticides in nursery runoff on affected water bodies of urban watersheds. Specific objectives are:

1). Characterize nursery runoffs by examining levels and makeup of suspended solids and DOM and the association of bifenthrin with these components, and correlate runoff profiles with time, seasons, and on-site activities.

2). Investigate influence of suspended solids and DOM on the bioavailability and aquatic toxicity of bifenthrin in runoff.

3). Understand the persistence and partitioning of bifenthrin in nursery-derived sediment, and predict the scale and duration of the impact of runoff-borne pyrethroids on receiving water bodies of urban watersheds.

Procedure

1). Phase Fractionation of Pyrethroids in Runoff

Detailed information can be found in the publication "Phase fractionation of pyrethroids in runoff and stream water" (*Environmental Toxicology & Chemistry* 2004, 23: 7-11). Briefly, we developed and used a solid-phase microextraction (SPME) method to detect the freely dissolved phase of selected pyrethroids in the water samples. By comparing SPME-measured concentrations with total chemical concentrations determined following exhaustive solvent extraction, the relative distribution of pyrethroids in various runoff samples was quantified.

2). K_d Measurement by Solid Phase Microextraction (SPME)

Adsorption of a chemical to the solid phase is expected to greatly affect its mobility as well as bioavailability to non-target organisms. Traditionally, adsorption is measured using the batch equilibration method that involves analysis of the aqueous phase concentration by solvent extraction. However, we hypothesized that for strongly adsorbing compounds such as pyrethroids, this procedure may give erroneous estimation of K_d, as small amounts of fine particles and dissolved organic matter (DOM) in the aqueous phase may greatly enhance the aqueous phase concentration or decrease K_d. In this study we used the solid-phase microextraction (SPME) method to demonstrate an improved approach for determining K_d for pyrethroid compounds. We used bifenthrin and permethrin as model pyrethroids, and measured K_d from adsorption isotherms for three sediments as well as from *in-situ* field sediment samples. K_d was measured using the conventional method, as well as using SPME for the same sediment samples and compared. Detailed information may be found in the publication "Evaluation of K_d

underestimation using solid phase microextraction" (*Environmental Science & Technology*, 2003, 37: 5597-5602).

3). Microbial degradation in water and sediment

Degradation of pyrethroids in sediment affects their potential to move offsite into surface streams and their exposure to aquatic organisms. Degradation of pyrethroids is not well understood in the sediment environment. In this study, we used previously contaminated runoff sediments from a nursery site and isolated 56 of pyrethroid-degrading bacteria strains. Six of the isolated strains were further evaluated for their ability to transform bifenthrin and permethrin in the aqueous phase, and bifenthrin in the sediment phase. Detailed information on the procedure and treatments may be found in the publication "Microbial transformation of pyrethroid insecticides in aqueous and sediment phases" (*Environmental Toxicology & Chemistry*, 2004, 23: 1-6).

4). Distribution and persistence in runoff sediments

Movement of pyrethroids in runoff to downstream surface streams depends closely on their distribution and persistence in runoff sediments. Prolonged persistence results in enhanced risks for offsite transport. In this study, we characterized the spatial distribution and persistence of bifenthrin (BF) and permethrin (PM) in the sediment along a 260-m runoff path at a commercial nursery site. Total chemical concentration as well as apparent adsorption coefficient K_d were measured in sediment samples taken from five locations along the runoff channel following phase separation and solvent extraction. In addition, the persistence of pyrethroids in the sediment phase was determined under aerobic and anaerobic conditions and at two different temperatures (20 and 4 °C). The remaining chemical concentration was measured after exhaustive solvent extraction. Half-life in days was estimated by fitting pesticide concentrations as a function of time. Details on the procedure and treatments may be found in the publication "Distribution and persistence of synthetic pyrethroids in runoff sediments" (*J. Environmental Quality*, 2005, 34: 836-841).

5). Effect of suspended solids on pyrethroid bioavailability

Runoff and surface stream effluents commonly contain suspended solids. Adsorption to suspended particles and the associated dissolved organic matter (DOM) may significantly decrease the freely dissolved concentration of a hydrophobic compound and hence its availability to aquatic organisms. In this study we evaluated phase distribution and bioaccumulation of two synthetic pyrethroids, bifenthrin and permethrin, in water samples containing suspended solids from different source sediments. The phase distribution was evaluated using the previously developed SPME method. The bioavailability was determined after examining inhibitory effects of suspended solids to bioaccumulation of ^{14}C-labelled pesticides by the aquatic invertebrate *Daphnia magna*. Detailed information on the procedure and treatments may be found in the publication "Effect of suspended solids on bioavailability of synthetic pyrethroid insecticides" (*Environmental Toxicology & Chemistry*, 2006, June issue, In press).

Results

1). Phase fractionation of pyrethroids in runoff

Phase distribution of bifenthrin and permethrin was evaluated in previously contaminated runoff samples. For the same runoff water, whole effluent extraction consistently gave much higher bifenthrin or permethrin concentrations when compared to the SPME approach. At the inlet of a runoff channel, concentrations determined by the whole effluent extraction method were 3.7-4.6 times of those measured by SPME. At the channel outlet, the concentrations detected by the whole effluent extraction method were 7.3-10.0 times of those obtained by SPME. In terms of mass distribution, 22-27% of the overall SPs was in the freely dissolved phase for the inlet runoff sample, and 10-14% in the outlet runoff sample. These results suggest that phase distribution of pyrethroids occurred in the field runoff effluents, and that only a fraction of the overall SPs existed in the freely dissolved phase. While SPME was capable of detecting the freely dissolved phase, the whole effluent extraction method measured for both the freely dissolved phase *and* the adsorbed phases. The distribution of SPs between the freely dissolved and adsorbed phases in runoff effluents has implications for interpreting water quality impacts and selection of valid sampling protocols. For instance, the LC50 for bifenthrin against *Ceriodaphnia dubia*, an aquatic invertebrate species that is commonly used for toxicity assays, is 0.078 $\mu g\ L^{-1}$. If the whole sample is extracted by a whole effluent extraction method, as practiced in monitoring studies, the concentration in the outlet runoff, at $0.123 \pm 0.011\ \mu g\ L^{-1}$, would indicate toxicity. However, SPME sampling results in a concentration of $0.012 \pm 0.001\ \mu g\ L^{-1}$, which would indicate little or no toxicity to *C. dubia* by bifenthrin. When monitoring is used for enforcing water quality permits, analysis by the whole effluent extraction method would suggest toxicity, while analysis by SPME would indicate compliance.

2). K_d Measurement by Solid Phase Microextraction (SPME)

The K_d values measured for the same sediment but with different methods for detecting the aqueous phase concentration were statistically compared at $\alpha = 0.95$. In each of the pesticide-sediment combinations, the K_d given by SPME was significantly greater than that by the conventional method. For bifenthrin, K_d determined by SPME was 0.6 – 2.6 fold greater than that by the conventional method; the increase was 1.7 – 4.4 fold for *cis*-permethrin, and 0.9 – 2.1 fold for *trans*-permethrin. K_d was further measured by the two different methods using *in situ* sediment samples. Again, SPME consistently gave K_d values significantly greater than those obtained by the conventional method. Compared to adsorption on the creek and field sediments, underestimation of the K_d by the conventional method was frequently greater for nursery runoff sediments, with the difference ratio ranging from 3.6 to 21.7. Underestimation by the conventional method was attributed to adsorption to DOM that was not excluded from the aqueous phase by centrifugation. The degree of underestimation was dependent on the source and amount of DOM, and may be generally significant for compounds that have organic carbon-normalized adsorption coefficient $K_{OC} > 10^4$. For bifenthrin and permethrin, K_{OC} estimated by SPME was generally $> 1\times10^6$, which was substantially greater than values reported in the literature. This suggests that the bioavailability or aquatic toxicity of pyrethroids in runoff or sediment may be significantly less than previously predicted.

3). Microbial degradation in water and sediment

In the aqueous phase, bifenthrin was rapidly degraded by strains of *Stenotrophomonas acidaminiphila*, and the half-life was reduced from >700 h to 30-131 h. Permethrin isomers were degraded by *Aeromonas sobria*, *Erwinia carotovora*, and *Yersinia frederiksenii*. Similarly to bifenthrin, the half-life of *cis*- and *trans*-permethrin was reduced by ~10 fold after bacteria inoculation. However, bifenthrin degradation by *S. acidaminiphila* was significantly inhibited in the presence of sediment, and the effect was likely caused by strong adsorption to the solid phase. Bifenthrin half-life was 343-466 h for a field sediment, and increased to 980-1200 h for a creek sediment. Bifenthrin degradation in the inoculated slurry treatments was not greatly enhanced when compared to the non-inoculated system. Therefore, although pyrethroid-degrading bacteria may be widespread in aquatic systems, adsorption to sediment could render pyrethroids unavailable to the degraders, thus prolonging their persistence.

4). Distribution and persistence in runoff sediments

Pesticide concentrations generally increased with increasing distance downstream from the source. For instance, while bifenthrin concentration was 0.33 mg kg^{-1} in the sedimentation pond, it increased to 2.27 mg kg^{-1} at 104 m downstream from the source, and further to 8.47-10.64 mg kg^{-1} at 145 m and beyond. Similar distribution patterns were also observed for *cis* and *trans* isomers of permethrin. Using the concentration for the sedimentation pond as the reference value, the relative enrichment ratio (ER) was calculated for the different locations. Assuming ER was 1.0 for the sedimentation pond, ER for bifenthrin increased to 6.9 at 104 m, and further to 25.7-32.2 after 145 m. The ER for *cis* and *trans* isomers of permethrin also increased with increasing distance from the source, although at rates smaller than those for bifenthrin. For the same compound, the measured K_d invariably increased with the distance from the sedimentation pond. Using the pond as a reference point, K_d for bifenthrin increased by ~8 times at 104 m, and by 22.7-43.9 times after 145 m. Increases in K_d were also observed for permethrin isomers. Concurrent to increases in ER and K_d in the sediment phase, sediment organic carbon content (OC) and clay content also increased with distance from the source. The ER for sediment OC increased to 3.6 at 104 m, and further to 7.0-9.8 after 145 m. The ER for sediment clay fraction also increased to 3.8-4.6 for the 145-210 m section. This analysis suggests that sediment movement in the drainage channel was a selective process, in which organic matter and chemical-rich fine particles transported downstream preferentially in relation to the organic matter and chemical-poor large particles. Enrichment of pyrethroids during runoff may have several important implications. First, although the concentration of a pyrethroid compound in the source may be low, the significant enrichment potential may result in high pesticide levels entering the surface water during irrigation or storm induced runoff. The significant increases in K_d over a short distance as observed in this study suggest that although the total pesticide concentration is enhanced due to sediment enrichment, the bioavailability may simultaneously decrease. In addition, as evident from this study, sediment is likely the predominant carrier for compounds such as BF and PM. Therefore, sedimentation-based mitigation practices may be valuable for reducing surface water contamination by pyrethroids through runoff. However, because sedimentation ponds or similar practices are effective only at retaining large particles, practices aiming at reducing transport of fine particles may be essential for preventing pyrethroids from entering surface water streams.

At 20 °C, bifenthrin exhibited similar persistence in the different sediments, with half-life ranging 428-483 days, or 12-16 months. Degradation of permethrin under the same conditions was significantly faster than that of bifenthrin. The half-life of *cis*-permethrin in the sediments was 98-142 days (or 3-4.7 months), and that of *trans*-permethrin 60-312 days (or 2-10 months). At 4°C, persistence of both bifenthrin and permethrin was significantly prolonged. The half-life of bifenthrin increased to 764-1950 days (or 25-65 months), which represented an increase of 1.6-4.5 times as compared to the same treatments at 20 °C. The half-life of both permethrin isomers also increased significantly, with half-life ranging 152-297 days (or 5-10 months) for *cis*-permethrin and 490-2150 days (or 16-72 months) for *trans*-permethrin. Degradation of bifenthrin was generally enhanced under anaerobic conditions when compared to the aerobic treatments. The half-life of bifenthrin was 251-498 days (or 8-16 months) for treatments at 20°C, and 277-470 days (or 9-16 months) for treatments at 4°C. However, degradation of *cis*-permethrin was consistently inhibited under anaerobic conditions when compared to the aerobic treatments, with half-life extended to 209-380 days (or 7-13 months) at 20 °C, and to 148-450 days (or 5-15 months) at 4 °C. Overall, the selected pyrethroids exhibited moderate to long persistence in the sediments under either aerobic or anaerobic conditions. The long persistence of bifenthrin implies that there is a greater possibility for bifenthrin to be transported into downstream surface waterbodies during active runoff.

5). Effect of suspended solids on pyrethroid bioavailability

Uptake of ^{14}C-bifenthrin or permethrin by *Daphnia magna* after 24 h consistently decreased with increasing levels of suspended solids in the 0-200 mg L^{-1} range. The trend of decrease was closely mimicked by pesticide accumulation on polydimethylsiloxane (PDMS) fibers exposed under the same conditions, and the ratio of body residues in *D. magna* and the concentration detected in the PDMS fiber was consistently around 2.4. Regression analysis showed that the pesticide adsorbed on particles or DOM was completely unavailable to *D. magna* for uptake during the 24-h exposure. The relative contribution of particles and DOM to the reduced bioavailability depended on the organic matter content and texture of the source sediment. The influence from particles was predominant for sandy sediments, but contribution from DOM became comparable to or even greater than particles when the organic matter content of the source sediment was ≥ 1%. Results from this study suggest that the inhibitory effects of suspended solids on bioavailability should be considered when monitoring runoff and surface water effluents for synthetic pyrethroids. The proposed PDMS method is simple and inexpensive, and may serve as an effective option for obtaining ecotoxicologically relevant concentrations.

Conclusions

The following conclusions may be drawn from results obtained through this project:

1). Pyrethroid insecticides are strongly adsorbed to sediment particles as well as dissolved organic matter. The adsorption capacity was found to be significantly greater than previously reported. This implies that bioavailability of pyrethroids should be even less than previously predicted.
2). In runoff effluents, a significant fraction of the total chemical concentration is associated with the suspended solids and dissolved organic matter. This suggests that bioavailability or toxicity of pyrethroid insecticides in runoff is less than predicted from the total concentration that is currently measured. To better assess effluent toxicity, the freely dissolved concentration should be measured. This project led to the development of a selective method (solid-phase microextraction, or SPME) that may be used for measuring the free pyrethroid concentration.
3). Presence of suspended solids significantly decreased the uptake of pesticides by the aquatic invertebrate *Daphnia magna*, validating the above hypothesis.
4). Pyrethroids generally show moderate to long persistence in runoff sediment. The long persistence of bifenthrin suggests that it has a high risk for contaminating surface streams that receive runoff flows. There are other pyrethroids that may behave like bifenthrin, and they may also have enhanced runoff risk.
5). The strong adsorption of pyrethroids by sediment suggests that management practices that reduce sediment movement should be effective in reducing the load of pyrethroids in runoff and should be tested.

List of publications

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