

## Sorption Isotherms and $K_{oc}$ s Estimation of Pyrethroids in Sediments

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Laboratory sorption isotherm batch studies have been attempted to elucidate interaction of synthetic pyrethroids (bifenthrin and permethrin) with sediments and their fractions. As a nonlinear isothermal model, the Freundlich equation was applied to sorption results obtained from sediments to investigate the relationship between synthetic pyrethroids and sediments containing different amounts of organic carbon. Results demonstrated that the sorption capabilities of bifenthrin and cis- and trans-permethrin was in the order of bifenthrin, cis-permethrin and trans-permethrin, respectively, indicating that adsorbed bifenthrin was the most stable followed by cis- and trans-permethrin in all sediments. Their sorption capability was closely related to organic carbon contents in sediments. Higher sorption was observed in sediments containing higher organic carbon contents. Sorption study extended into the fractions, clay and humic acids, extracted from a sediment, indicated that higher sorption capacity in humic acids occurred than in the clay of both examined bifenthrin and permethrin. This study demonstrates the sorption of synthetic pyrethroids with sediments, and will help in the understanding of the transport and fate of synthetic pyrethroids existing in field sediments.

Key Words: Sorption, Bifenthrin, Permethrin, Freundlich equation

### 1. Introduction

Nursery production industry plays a critical role in California, USA. The heavy use of pesticides and fertilizers were employed in nurseries, which were coupled with intensive overhead sprinkler and drip irrigation. This phenomenon drives discharges of pesticides, nutrients and sediments in runoff. Various types of pesticides including diazinon, chlorpyrifos, bifenthrin, permethrin, and melathion, have been found in nursery runoffs and in adjacent creeks.<sup>1)</sup>

Pesticides differ greatly in their tendency to be retained by sediments. Once in sediment, pesticides also degrade at different rates. Synthetic pyrethroids are extreme examples of

persistent and sediment-affinitive pesticides.<sup>1)</sup> In recent monitoring studies by DPR (Department of Pesticide Regulation), pyrethroid residues were dramatically enriched in nursery-derived sediments, often to the levels that were thousands of times higher than those in the overflowing runoff water. In addition, it is known that aged pesticide residues can become extremely persistent, because pesticide molecules tend to migrate to the inside of soil particles and become permanently entrapped.<sup>2)</sup>

Bifenthrin and permethrin, pyrethroid insecticides used to control fire ants in potting mix and flies, were used as sorbates in this study because they are commonly used pesticide in nursery sites. These synthetic pyrethroids are considered as replacements to some organophosphate insecticides and are strongly absorbing to soil or sediment but hardly soluble in water.<sup>3)</sup> Organophosphates, may drain through potting media upon irrigation, and move offsite after dissolution in water. Among organophosphates

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compounds, especially, those which have high water solubility, can travel over a large distance in runoff because of their low adsorption capability.<sup>2)</sup> Meanwhile, pyrethroids may move offsite and only travel over a small distance, likely being adsorbed by solid materials such as fine clay particles, because these compounds have low water solubility and strong affinity to soil or sediment.

Soil and sediment play a critical role as environmental sinks to alleviate the impact of pollution issues. The phenomenon of the pesticides has been invoked and extensively studied by many investigators in both the laboratory and the field. Sorption has the effect of reducing the concentration of chemicals in solution. Due to a strong sorption phenomenon of pyrethroids on solid materials, our attention for understanding of sorption and desorption behavior in different types of sediments should be more focused nowadays. Extensive studies for the understanding of sorption/desorption behavior of organophosphate insecticides or herbicides have been attempted.<sup>4-9)</sup> However, sorption and desorption characteristics of synthetic pyrethroids in soil with respect to soil compositions such as clay and humic acids and their fractions have not been extensively studied.<sup>10,11)</sup>

The objectives of this study were to determine the sorption isotherm and to estimate  $K_{oc}$  values of synthetic pyrethroids, bifenthrin and permethrin, in 3 types of sediments composed of different soil compositions, and their fractions, clay and humic acids. An understanding of sorption behavior in sediments may be helpful in controlling pesticide runoff effectively. We hope this study can provide more insights for and a better understanding of the sorption of bifenthrin and permethrin in solid phase.

## 2. Materials and Methods

### 2.1. Sorbents preparation

The laboratory batch studies were conducted using three different types of sediments collected from Nursery field (NF), San Diego (SD), and Bolita Creeks (BO) which located in close to nursery sites in Southern California, USA. The sediments were passed through a 2-mm sieve after using a mortar and pestle to break up clods. Obvious vegetable matter such as wood fragments and leaf debris was removed. The sieved sediment was air-dried, mixed thoroughly, and then stored in a plastic bag until used. Samples from these sediments were methanol-extracted, analyzed and found to be free of the test compounds. Soil analyses were performed as per the standard methods in the DANR (Division of Agricultural and Natural Resources) The physical and chemical characteristics of sediments analyzed by laboratory in University of California, Davis are presented in Table 1. The sediment from the NF, SD, and BO were classified using USDA(U.S. Department of Agriculture) soil classification method and results were listed in Table 1. The texture of them were characterized as sand, loamy sand, and loam, respectively. The air-dried soil had gravimetric moisture content of less than 2%, organic carbon ranging from 0.13 to 1.04 %(by weight), and pH ranging from 7.1 to 7.3.

### 2.2. Chemicals

Two pyrethroids were selected for this batch study: bifenthrin(BF) and permethrin(PM). The bifenthrin (>98% purity) and permethrin (>98% purity) were purchased from Chem Service (West Chester, PA). Ethyl acetate, hexane and acetone (99% purity, pesticide grade) were purchased from Fisher Scientific (Pittsburgh, PA) and used as solvents for liquid as well as

Table 1. Physical and chemical analysis of soils used in this study

Sediment	Soil Texture(%)			OC (%)	pH	CEC (meq/100g)
	Sand	Silt	Clay			
NF	86	7	7	0.13	7.1	8.4
SD	76	15	9	1.04	7.1	27.0
BO	47	34	19	0.73	7.3	37.8

Note: SF, Strawberry Field; SD, San Diego Creek; BO, Bolita Creek

solid phase.

### 2.3. Sorption isotherm studies

#### 2.3.1. Sediment Phase

All sorption isotherms were run according to the batch equilibrium technique<sup>12)</sup> at ambient temperature in 250 mL glass centrifuge glass tubes with aluminum wrapped rubber caps. The background solution consisted of 0.01M CaCl<sub>2</sub> solution containing bifenthrin at 0.04, 0.06, 0.08, 0.10 mg/L or Permethrin (sum of two isomers) at 0.08, 0.12, 0.16, 0.20 mg/L. Low initial concentrations were used to accommodate the low water solubility of these compounds. The water solubility of bifenthrin and permethrin are 0.10 and 0.20 mg/L, respectively. Due to low solubility of bifenthrin and cis-, trans-permethrin, they were mixed at high concentrations in acetone before being added (did not exceed 0.1% by volume) to the background solution. According to the sorption kinetic study previously conducted (data not shown), adsorption of synthetic pyrethroids were completed in 24 hours by reaching equilibrium. Therefore, prepared solutions containing bifenthrin and cis-, trans-permethrin, with the concentrations described above, were mixed with all sorbents on a platform shaker under low speed for 24 hours. Based on initial kinetic studies (not shown), bifenthrin and cis-, trans-permethrin were mixed with all sorbents for 1 day to reach apparent equilibrium.

For the experimental treatments, 2 g of dried soils and 180 ml of electrolytes composing of 0.01M CaCl<sub>2</sub> were prepared and added into each 250 mL-capacity centrifuge glass-tubes. The use of a relatively large solution to solid ratio was necessary because the aqueous phase concentration at equilibrium was very low due to strong adsorption. All samples were run in triplicate. After mixing, glass tubes were centrifuged at 7,000g for 30 min, followed by supernatant collection. The collected supernatant was then extracted with 50 ml of ethyl acetate three times in a 1-L glass separatory funnel and then went through the concentration process by rotary evaporator (Büchi 461, Switzerland) by setting up the water bath temperature at 60°C. 5mL of hexane and acetone (1:1, v:v) was used to extract dried examined substances and

analyzed in GC-ECD. Meanwhile, the residual amounts of water in the soil phase were removed by adding 10g of anhydrous Na<sub>2</sub>SO<sub>4</sub>. The soil phase was then extracted with a hexane: acetone (1:1) solution by shaking for an hour on the platform shaker.

#### 2.3.2. Clay and humic acid phase

Clay and humic acids were extracted from the sediments collected from SD and BO. The procedures for extracting clay and humic acids are well described in Methods of Soil Analysis.<sup>13)</sup> 0.2 g of dried solids and 40ml of electrolyte were added into 40ml capacity Teflon centrifuge tubes. The procedures are the same as the one conducted with the sediment phase as described in the previous section. All samples were treated in triplicate. After mixing, separation of supernatant fraction with solid phase was accomplished by centrifuging at 7000g for 30 min, followed by supernatant removal. The supernatant was collected and extracted with 20 ml of ethyl acetate three times in a 0.25 L glass separatory funnel and then went through the concentration process by rotary evaporator (Bchi 461, Switzerland) by setting up the water bath temperature at 60°C. 5mL of a hexane and acetone mixture(1:1, v:v) was added and analyzed in GC-ECD. Meanwhile, the soil phase was extracted with a hexane: acetone (1:1) solution and 5 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> when necessary for the removal of residual amounts of water.

### 2.4. Data analysis

Extensive laboratory batch studies have shown that pesticide sorption is often described by the empirical Freundlich isotherm as shown in the following equation, and this nonlinear sorption has been known to significantly affect macroscopic transport behavior.<sup>14)</sup>

$$C_s = K_f \cdot C_e^{1/n}$$

where  $C_e$  is pesticide concentration in solution phase ( $\mu\text{g mL}^{-1}$ ),  $C_s$  is pesticide concentration in sorbed phase ( $\mu\text{g g}^{-1}$ ),  $K_f$  is the Freundlich distribution coefficient [ $(\mu\text{g g}^{-1}) (\text{mL } \mu\text{g}^{-1})^n$ ], and  $n$  is the dimensionless Freundlich isotherm exponent.

Table 2. Isotherm parameters and estimated organic carbon coefficients (K<sub>oc</sub>) for bifenthrin and permethrin sorption by various types of sediments

Sedi-ments	Bifenthrin				Permethrin							
					Cis-Permethrin				Trans-Permethrin			
	K <sub>f</sub> <sup>*</sup>	n	R <sup>2</sup>	K <sub>oc</sub> <sup>**</sup>	K <sub>f</sub> <sup>*</sup>	n	R <sup>2</sup>	K <sub>oc</sub> <sup>**</sup>	K <sub>f</sub> <sup>*</sup>	n	R <sub>2</sub>	K <sub>oc</sub> <sup>**</sup>
NF	3714	0.76	0.93	2.9E6	1803	1.05	0.94	1.4E6	1524	0.95	0.95	1.2E6
SD	33343	1.06	0.97	3.2E6	26303	0.95	0.98	2.5E6	26607	0.95	0.98	2.6E6
BO	12134	1.31	0.89	1.7E6	8054	0.94	0.96	1.1E6	6653	1.09	0.94	9.1E5

\* : mL/g soil ; \*\* : mL/g OC

Table 3. Isotherm parameters for bifenthrin and permethrin sorption in clay and humic acids extracted from the sediments used in this study

Sorbents	Bifenthrin			Permethrin					
				Cis-Permethrin			Trans-Permethrin		
	K <sub>f</sub> <sup>*</sup>	n	R <sup>2</sup>	K <sub>f</sub> <sup>*</sup>	n	R <sup>2</sup>	K <sub>f</sub> <sup>*</sup>	n	R <sup>2</sup>
SD-Clay	9.8E3	0.62	0.60	2.2E3	0.42	0.91	5.9E3	0.48	0.92
BO-Clay	5.8E5	1.09	0.81	1.6E6	1.39	0.92	1.0E5	0.76	0.97
BO-HA	1.4E7	1.71	0.98	3.3E5	1.13	0.96	6.2E5	1.10	0.96

\* : mL/g soil

## 2.5. 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 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 oC; detector temperature, 300 oC; oven temperature, initially 150 oC for 1.0 min, ramped to 280 oC at 15 oC min<sup>-1</sup>, and kept at 280 oC for 5.0 min. Samples were introduced in the splitless mode. The identification of pyrethroids was carried out via comparison of retention times of peaks in the samples relative to the standard with relative retention times of reference chemicals. The calibration curve was prepared and plots were linear with a correlation coefficient of 0.99 or higher.

## 3. Results and Discussion

### 3.1. Sorption isotherm

The Freundlich equation was fit to the observed sorption data by linear regression of log-transformed data (Tables 2, 3 and Fig. 1 through 4). The Freundlich constants provide

rough estimates of the sorbent capacity and the nature of sorption, respectively. The intercept, K<sub>f</sub>, gives an indication on the extent of sorption, and it is valuable for comparing the sorption of different pesticides on various sorbents. The data in Table 2 and 3 show the effect of soil type and nature of the chemical on the magnitude of K<sub>f</sub>.

As shown in table 1, three different types of sediments containing different organic carbon contents were used for the sorption isotherm study. The sediment from SD contains the highest amounts of OC (Organic carbon; %), followed by BO and NF. The sorption behaviors of bifenthrin in sediments were demonstrated, and sorption relations were closely related to OC (%) by showing the highest affinity in SD sediment followed by BO and NF on the same order of OC contents. The K<sub>f</sub> value in SD sediments was 10 times higher in magnitude than that of the sediment in the nursery field(NF). This phenomenon was again observed in sediments contaminated by permethrin through determining that the highest K<sub>f</sub> values are in the SD sediment (Fig. 2).

As shown in Table 2, bifenthrin showed the highest sorption capabilities in all sediments, followed by cis and trans-permethrin, respective-

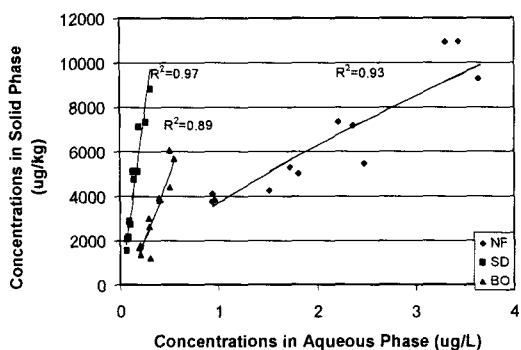
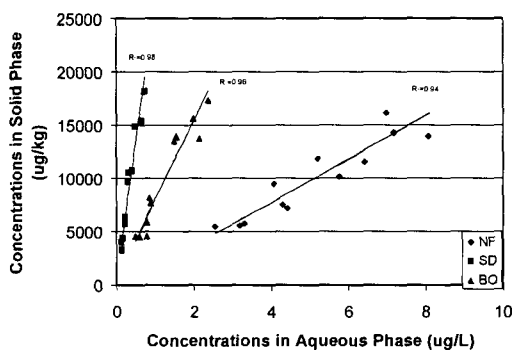


Fig 1. Bifenthrin sorption isotherm in sediments.

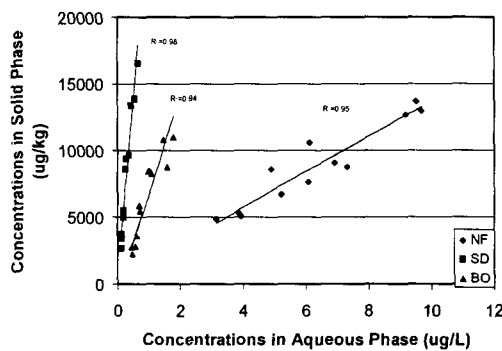
ly. This result supports that of previous findings.<sup>15)</sup> However, it does not always hold true in clay and humic acid fractions extracted from sediments (Table 3). Although bifenthrin did not follow a linear isotherm in SF and BO sediments ( $n = 0.755$  in SN,  $n=1.308$ ), the SD sediment ( $n=1.059$ ), as well as both isomers in permethrin, did follow linear isotherms, respective-

ly, in all sediments ( $0.939 < n < 1.093$ ).

For the fractions consisting of clay and humic acids or extracted from SD and BO, the sorption phenomenon was observed. A higher capacity occurred in HA than in the clay fractions of both examined substances (Table 3). The linear sorption isotherms did not occur in bifenthrin -contaminated sediments except for the clay fraction in BO, yielding 1.09 as the  $n$  value. In addition, non-linear sorption isotherm patterns were also observed in all sediments. The sorption capability in clay and humic acid fractions did not follow the trends found in sediments, as characterized by a higher sorption behavior in trans-permethrin than in *cis*-permethrin. However, a higher sorption was observed in the humic acid fraction in contrast to the clay fraction, except for *cis*-permethrin.



(a)



(b)

Fig. 2. Permethrin sorption isotherm in sediments. (a) *cis*- (b) *trans*-.

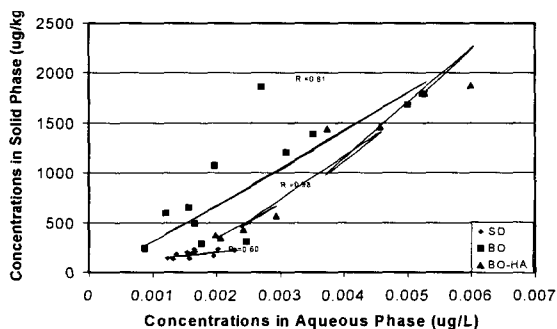


Fig. 3. Bifenthrin sorption isotherms in clay and humic acid fractions extracted from San Diego and Bolita creeks in USA.

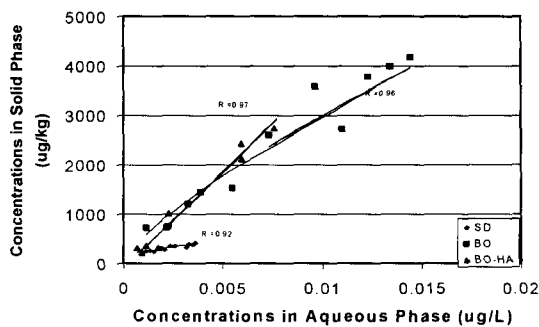


Fig. 4. Permethrin sorption isotherms in clay and humic acid fractions extracted from San Diego and Bolita creeks in USA.

### 3.2. $K_{oc}$

As shown in Table 2, the average sorption behavior for a given chemical is many times that for the sandy NF. This variation among the three sediments is an expression of the high positive correlation between sorption and soil OC content, which has been reported by many investigators.<sup>5,7,9)</sup> Hamaker and Thompson<sup>16)</sup> introduced a relationship for calculating sorption constants based on a soil OC content instead of the total soil mass. This relationship is expressed by dividing the sorption constant,  $K_f$ , by the OC content of soil.

$$K_{oc} = K_f / (\%C / 100)$$

The  $K_{oc}$ , organic carbon partition coefficient, values for bifenthrin ranged between 1662176 and 3206023 mL/g, while values for cis-permethrin were 1103257 and 2529103 mL/g, and 911332 and 2558389 mL/g for trans-permethrin. Most literature  $K_{oc}$  values predict that bifenthrin would be more highly sorbed than permethrin, which is supportive of the findings of the study.<sup>15)</sup> However, there were no distinctive variations in the  $K_{oc}$  values in isomers of permethrin. The reason the  $K_{oc}$  values in tested sediment types displayed a two fold variation may be attributed to the experimental artifacts caused from measurements in the aqueous phase experiment with the solvent extraction process because of high affinity to solid materials. This drives the distribution of coefficients values lower than they should be. Therefore, extreme caution must be taken while in the field obtaining measurements used in the determination of  $K_f$  values.

### 4. Conclusions

The batch sorption studies of 3 different sediments were conducted to determine the distribution of the pesticides in the presence of soil particles. The described results of this paper yields detailed information on the sorption behavior of the two pyrethroids studied. Due to high sorption affinity to soil particles, the distribution of insecticides such as bifenthrin and permethrin can be regarded as important issues in the presence of soil particles. As

expected, sorption capability was affected by organic carbon contents and soil composition with measured  $K_f$  values for bifenthrin and permethrin. The sediments collected from SD, containing the highest organic carbon contents, showed the highest  $K_f$  values for both bifenthrin and isomers of permethrin as followed by sediments from BO and NF.

This study gives insight into pyrethroids behavior in various types of sediment, especially for the sediments originating from runoff during irrigation activities at nursery sites, which heavily apply pesticides. Their strong affinity to soil particles draws attention to addressing the issue of how to remediate pyrethroids- contaminated sediment. This issue is part of ongoing research into the mitigation of pesticides at nursery sites located in Southern California .

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