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Effects of Dissolved Organic Matter on Permethrin Bioavailability to *Daphnia* Species

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Synthetic pyrethroids are widely used insecticides in both agricultural and urban environments. Recent studies show frequent appearances of pyrethroid residues in runoff effluents and sediments, which stimulated concerns over the potential ecotoxicological implications. Pyrethroids are known to have two contrasting characteristics, high aquatic toxicity and strong affinity for the solid phase, that may negate the actual toxicity in a multiphased system. This study evaluated the effect of dissolved organic matter (DOM) on the pyrethroid uptake by and acute toxicity to water-column invertebrates using permethrin as a model compound. During the bioassays, the freely dissolved permethrin concentration was simultaneously measured using poly(dimethylsiloxane) (PDMS) fibers as a biomimetic surrogate. The presence of DOM consistently decreased permethrin uptake and increased its LC_{50}. For instance, compared to the DOM-free treatment, the LC_{50} of permethrin to *Ceriodaphnia dubia* in a pond water containing DOM at 10 mg L^{-1} increased from 0.56 to 1.03 μg L^{-1}, whereas the bioaccumulation factor by *Daphnia magna* decreased by 56%. Permethrin accumulation on the PDMS fiber closely mimicked permethrin uptake by *D. magna*. Statistical analyses suggest that permethrin associated with DOM was completely unavailable to *D. magna* or *C. dubia*. The effect of DOM on permethrin bioavailability appeared to depend also on the source of the DOM. These results indicate that the inhibitory role of DOM should be considered in the development of toxicologically relevant water quality limits and in monitoring protocols for permethrin and other pyrethroids in runoff effluents and surface streams that ubiquitously contain DOM.

KEYWORDS: Bioavailability; biomimetic sampling; synthetic pyrethroids; dissolved organic matter; effluent toxicity

INTRODUCTION

Synthetic pyrethroids are widely used for insect control in both agricultural and urban environments, and their use is expected to increase further as the use of some organophosphate products is being reduced. In California, permethrin has been the most heavily used compound in the pyrethroid family. In 2003, the recorded use of permethrin was 200 500 kg, which was substantially more than that of the second most used pyrethroid, cypermethrin (90 500 kg) (California Pesticide Use Reports, http://www.cdpr.ca.gov/docs/pur/pur03rep/03_pur.htm). Pyrethroids are generally known for their poor mobility in the environment because of their strong affinity for the solid phase (*1*). However, recent studies show that runoff or erosion may move pyrethroids into surface water (*2*−*7*). Among the pyrethroids found in sediment or runoff effluents, permethrin was detected more frequently than the other compounds, apparently due to its widespread use (*2*, *5*, *6*).

Pyrethroids commonly show high acute toxicity to water-column invertebrates in laboratory tests (*1*). For instance, the literature-cited LC_{50} value of permethrin to *Ceriodaphnia dubia* is ≈0.5 μg L^{-1} (*8*). However, natural surface water samples usually contain dissolved organic matter (DOM), and adsorption of permethrin by DOM may significantly decrease the actual toxicity by reducing the bioavailable concentration (*9*−*11*). Previous studies on this topic focused largely on the effect of bulk sediments or suspended solids (*3*, *12*, *13*). In the case when the role of DOM was evaluated, commercial sources of DOM (i.e., Aldrich humic acid) were used (*9*). However, studies with other hydrophobic compounds showed that Aldrich humic acid was characteristically different from naturally occurring DOM and may display a much different inhibitory effect than naturally occurring DOM (*11*).

A key to understanding the effect of DOM on ecotoxicological endpoints is to quantify the bioavailable or free concentration of the target chemical. Methods used to date for

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Table 1. Selected Properties of Dissolved Organic Matter-Containing Water Samples Used in This Study

DOM source	alkalinity (mg L^{-1})	hardness (mg L^{-1})	ammonia (mg L^{-1})	Cl^- (mg L^{-1})	DOC (mg L^{-1})
lake water	458 ± 4	418 ± 7	0.27 ± 0.12	0.67 ± 0.12	30.7 ± 0.3
pond water	352 ± 11	353 ± 3	<0.2	<0.2	10.9 ± 1.1
compost extract	181 ± 9	209 ± 16	0.23 ± 0.15	0.73 ± 0.12	444.1 ± 5.5

measuring the free chemical concentration in aqueous media have various limitations and are either time-consuming (e.g., membrane dialysis), disruptive to phase equilibrium (e.g., Tenax extraction), or compound-specific (e.g., fluorescence quenching) (*14*, *15*). Researchers recently introduced a modified solid-phase microextraction (SPME) method, in which disposable polymer-coated fibers were used as a biomimetic surrogate to estimate the free concentration (*14*, *16*−*18*). This method has been shown to closely predict bioavailable concentrations of hydrophobic chemicals (e.g., PAHs) in soils or sediments (*17*, *19*). In this study, we used permethrin as a model pyrethroid to determine if DOM at naturally occurring levels would significantly inhibit pyrethroid uptake by and toxicity to water-column invertebrates.

MATERIALS AND METHODS

Chemicals. ^{14}C-Carbonyl-labeled permethrin [3-phenoxybenzyl-(1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate; purity = 98%] with specific activity of 6.7×10^3 kBq μmol^{-1} was obtained from FMC (Princeton, NJ). The stock solution of [^{14}C]-permethrin was prepared in acetone at 1.0 mg L^{-1}. Nonlabeled permethrin (99.3%, FMC) was used in the toxicity tests. Stock solutions of permethrin were prepared at 100 mg L^{-1} in acetone and stored at 4 °C before use. Solvents and other chemicals used in the study were of GC or analytical reagent grade.

Test Water Samples. Surface water samples were taken from Lake Elsinore in Riverside County, California (lake water), and a small pond near the campus of the University of California in Riverside, CA (pond water). To simulate runoff effluents from sites such as nurseries and animal feedlots, aqueous extracts were prepared from a commercial compost (Earthgro, Marysville, OH). Briefly, 10 g of compost was stirred in 500 mL of deionized water for 1 h at 600 rpm, and the slurry was allowed to settle for 2 h. The overlying aqueous phase was removed and used as the crude compost extract. Before use, water samples and compost extracts were first passed through 1.0 μm glass fiber filters and then through 0.45 μm sterile nitrocellulose membranes (Fisher) to remove particulate organic matter. The organic matter remaining in the filtrate was defined as DOM in this study. The DOM-containing waters were stored in the dark at 4 °C before use. Selected characteristics of the water samples were measured (**Table 1**). Alkalinity, hardness, chlorinity, and ammonia concentration were determined with a standard test kit (La Motte, Chester Town, MD). Dissolved organic carbon (DOC) was determined on a TOC-VCSH/CSN analyzer (Shimadzu, Kyoto, Japan).

Test Organisms. Two freshwater invertebrates, *Ceriodaphnia dubia* and *Daphnia magna*, were used in this study. Both test organisms were purchased from Aquatic Biosystem (Fort Collins, CO) and cultivated in the laboratory for several months before use. *C. dubia* was cultivated in moderately hard water (MHW) and *D. magna* in reconstituted hard water (RHW). MHW was prepared in deionized water by adding the following salts on a per liter basis: $NaHCO_3$ (96 mg), $CaSO_4{\cdot}2H_2O$ (60), $MgSO_4$ (60 mg), and KCl (4 mg). The concentrations of all salts were doubled in RHW. Both MHW and RHW were aerated by continuous air bubbling before use. The photoperiod for all *C. dubia* and *D. magna* stock cultures and bioassays was 16/8 h light/dark, and the temperature was room temperature (21 ± 1 °C). During cultivation, all organisms were fed daily with 1 mL of a combination of yeast, cerophylla, and trout chow (YCT) and 3 mL of *Selenastrum capricornutum* (≈3.0×10^7 cells mL^{-1}) (Aquatic Biosystem, Fort Collins, CO).

Development of SPME Methods. Poly(dimethylsiloxane) (PDMS) coated fibers (430 μm diameter glass core with 35 μm PDMS coating) were purchased from Polymicro Technologies (Phoenix, AZ) and used to measure the freely dissolved concentration of permethrin in water samples. The coating volume of PDMS was 140 μg L^{-1} of fiber. Before use, PDMS fibers were cut into 3.0 cm pieces, rinsed with methanol and deionized water, and activated at 300 °C in a GC oven for 30 min. To evaluate the sorption kinetics of permethrin by the PDMS fiber, two 3.0 cm long PDMS fibers were equilibrated in 100 mL of aqueous solutions containing [^{14}C]permethrin at 0.2 μg L^{-1} in 125 mL wide-mouth glass jars. After 3, 7, 24, 48, 72, 96, and 168 h of exposure, PDMS fibers (four replicates) were removed, rinsed briefly in deionized water, and gently wiped with a moist paper towel. The PDMS fibers were directly placed in 6 mL of Ultima Gold cocktail (Packard BioScience, Meriden, CT) in glass scintillation vials and equilibrated for 24 h, and the ^{14}C activity was measured on a Beckman LS 5000TD liquid scintillation counter (Fullerton, CA). Preliminary experiments showed that the recovery of this direct measurement approach was >95% for the ^{14}C sorbed on the fiber.

A 24 h exposure time was used for the bioaccumulation experiments. An additional experiment was carried out to determine the partition coefficient (K_{PDMS}) of permethrin between the polymer and water phases under the test conditions. K_{PDMS} was essential for deriving the free permethrin concentration (C_w) from the pesticide concentration in the PDMS polymer phase (C_{PDMS}), as shown in the following relationship:

$$K_{PDMS} = C_{PDMS}/C_w \quad (1)$$

Aqueous solutions with different permethrin concentrations were prepared and used to equilibrate PDMS fibers for 24 h. Following the equilibration, PDMS fibers were removed and analyzed for ^{14}C activity to obtain C_{PDMS}. An aliquot of the aqueous solution was simultaneously removed for measuring ^{14}C activity to obtain C_w. K_{PDMS} was calculated using eq 1 after linear regression over the entire concentration range.

Bioaccumulation Experiments. The bioaccumulation tests were conducted with 100 mL of test solution in 125 mL wide-mouth glass jars with an exposure time of 24 h. Only *D. magna* was used in these tests due to its larger size compared with *C. dubia*. The filtered water samples and compost extracts were diluted with RHW to obtain samples with different [DOC] levels. The initial [DOC] levels were 0, 1.0, 5.0, 10, 20, and 30 mg L^{-1} for the lake water and compost extract and 0, 0.5, 1, 2, 5, and 10 mg L^{-1} for the pond water, with [DOC] = 0 serving as the DOM-free control. Four replicates were prepared for each concentration level. Each test vessel was spiked with [^{14}C]permethrin in acetone (acetone was <0.1 vol %) at concentrations determined through a range-finding experiment. The test solutions were equilibrated for 2 h to allow the test chemical to distribute between the aqueous and DOM phases. Preliminary experiments showed that partition of permethrin between DOM and the water phase reached an apparent equilibrium within 2 h.

Following the equilibration, two 3.0 cm activated PDMS fibers and six 7−14-day-old *D. magna* were simultaneously introduced into each vessel, and the test vessels were kept at room temperature for 24 h. After the exposure, PDMS fibers were removed and analyzed for C_{PDMS}, from which C_w was further obtained from eq 1. The organisms were recovered and rinsed with 10 mL of deionized water. The dry weight of the test animals was determined following 24 h of air-drying at room temperature. The dried animals were then combusted on an OX500 Biological Oxidizer (R. J. Harvey, Hillsdale, NJ), and the released ^{14}C was measured on the LSC. The measurement gave body residue (BR) based on dry tissue weight, from which the bioaccumulation factor (BAF) was calculated as the ratio of BR over the solution concentration.

Toxicity Experiments. The effect of DOM on the acute toxicity of permethrin was measured through 96 h static toxicity assays using *C.*

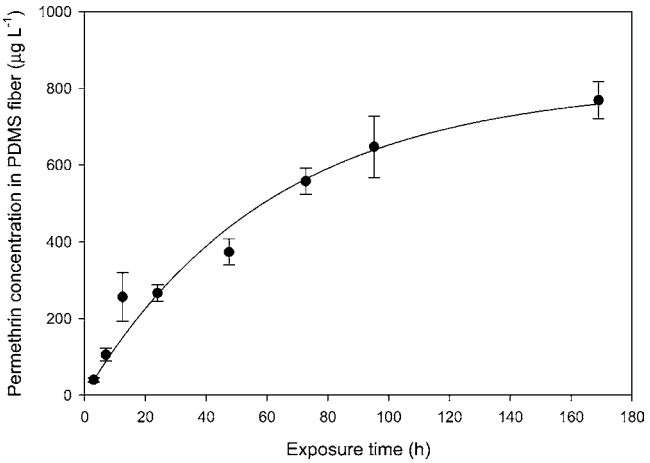

Figure 1. Sorption kinetics of permethrin on PDMS fibers in water at room temperature (21 ± 1 °C). Vertical lines are standard deviations of four replicates.

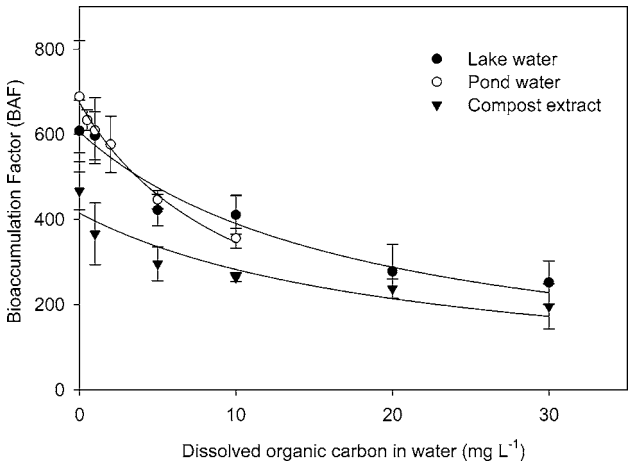

Figure 2. BAF of permethrin for *D. magna* after 24 h of exposure in test solutions containing DOM from different sources and at different levels. Vertical lines are standard deviations of four replicates.

dubia. The test conditions were consistent with the U.S. Environmental Protection Agency's guidelines for effluent toxicity tests (*20*). Briefly, test solutions with different [DOC] levels were prepared as described above, except that the medium was MHW. The initial permethrin stock solution was prepared at 1 mg L^{-1} in acetone/water (1:9, v/v) and was sequentially diluted with the test solution to achieve 0, 0.2, 0.4, 0.8, 1.2, 2.4, or 4.8 μg L^{-1} initial concentrations, with the 0 μg L^{-1} treatment serving as the permethrin-free control. The concentration range was determined through preliminary range-finding experiments to allow calculation of LC_{50}. Five *C. dubia* neonates (<24 h old) were transferred into 15 mL of test solution in 20 mL EPA glass vials. Four replicates were used for each concentration level. The organisms were fed with YCT and *S. capricornutum* for 4 h prior to the exposure and then 48 h into the exposure. The amount of food added was controlled so that the effect on permethrin partition, if any, was uniform among all treatments. After 24, 48, 72, and 96 h, the organisms were examined on a backlight (Hall Production, San Luis Obispo, CA), and the live animals were enumerated and recorded. LC_{50} was determined by probit analysis using ToxCalc (version 5.0) (Tidepool Scientific Software, McKinleyville, CA).

Pyrethroids are known to adsorb irreversibly to glass surfaces (*21*). In a preliminary experiment, the mass balance of permethrin in the test vessels was measured using [^{14}C]permethrin. Under conditions used for the bioaccumulation tests, 96−111% of permethrin remained in the test solution after 24 h of equilibration. Under conditions used for toxicity assays, 93−106% of the spiked permethrin was found in the test solution after 96 h of equilibration. The absence of adsorption to glass surfaces was likely due to the presence of DOM and/or ions in the test systems. Therefore, under the conditions used, adsorption to glass surfaces may be assumed to be negligible and would not affect the relative values of the measured C_{PDMS} (or C_w), BR, BAF, or LC_{50}. In addition, preliminary experiments showed that permethrin accumulation on the PDMS fibers was <5% of the total concentration, and therefore the use of PDMS fibers should not significantly disturb permethrin phase equilibrium in the test system.

RESULTS AND DISCUSSION

Partition of Permethrin between PDMS and Water. In SPME sampling, the PDMS layer acted as a nonpolar phase, allowing preferential partitioning of a hydrophobic chemical into the polymer phase via diffusion. As the exposure time increased, the amount of permethrin accumulated in the fiber increased (**Figure 1**). Accumulation of permethrin in the PDMS fiber as a function of time was fitted to a one-compartment model (*19*)

$$C_{PDMS} = C_m(1 - e^{-kt}) \quad (2)$$

where t is the exposure time, C_{PDMS} is the permethrin concentration in the fiber at time t, and C_m is the maximum permethrin concentration in the fiber. Accumulation of permethrin in PDMS was well described by eq 2 ($r^2 > 0.90$). The time at which the accumulation reached 95% of C_m was estimated to be 230 h. The long equilibrium time prevented the use of PDMS fibers under a steady state in this study. Consequently, a 24 h sampling interval was chosen to coincide with the animal exposure time in the bioaccumulation experiments. As sampling was conducted under nonequilibrium conditions, fiber exposure time was carefully controlled to ensure reproducible measurements.

The above method was used to sample water samples with different concentrations of permethrin. A linear relationship was found between C_{PDMS} and C_w over a wide concentration range (0.01−0.25 μg L^{-1}) with a slope of 1900 ($r^2 = 0.96$) (data not shown). The good linear correlation suggests that disposable PDMS fibers may be used to quantitatively determine the free permethrin concentration in aqueous samples. The slope of the regression line was K_{PDMS}, which was used to derive C_w from C_{PDMS} in the bioaccumulation experiments using eq 1.

Effects of DOM on Bioaccumulation of Permethrin by *D. magna*. Permethrin accumulation by *D. magna* consistently decreased with increasing [DOC] in all water samples (**Figure 2**). For instance, compared to the DOM-free treatment, the average BAF of permethrin based on the nominal concentration C_t decreased by 58, 47, and 58% in the lake water ([DOC] = 30 mg L^{-1}), pond water ([DOC] = 10 mg L^{-1}), and diluted compost extract ([DOC] = 30 mg L^{-1}), respectively. Concurrent analysis of permethrin accumulation in the PDMS fiber showed that C_{PDMS} decreased with increasing [*DOC*] in a trend similar to that of BAF (**Figure 3**).

In DOM-containing water samples, the freely dissolved permethrin concentration C_w may be related to the nominal or spiked concentration C_t via eq 3 (*22*)

$$C_w = \frac{C_t}{1 + K_{DOC}[DOC]} \quad (3)$$

where [DOC] is the dissolved organic carbon content of the aqueous sample and K_{DOC} is the DOC-normalized adsorption coefficient. Permethrin uptake by an organism is proportional to C_w and may be described by a relationship similar to that

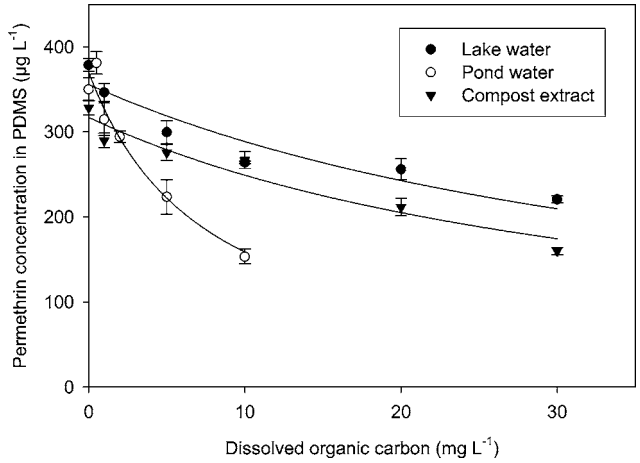

Figure 3. Permethrin accumulation on PDMS fibers exposed in test solutions containing DOM from different sources and at different levels. Vertical lines are standard deviations of four replicates.

given by Kukkonen et al. (*22*)

$$\mathrm{BAF} = \frac{\mathrm{BAF}_0}{1 + \alpha K_{\mathrm{DOC}}[\mathrm{DOC}]} \quad (4)$$

where BAF_0 is the BAF expected in the DOM-free control and α is a factor measuring the degree of availability of the DOM-adsorbed permethrin. The value of α may be determined by comparing eqs 3 and 4 after regression of measured data. If $\alpha = 1$, eq 4 reduces to a form consistent with eq 3, which suggests that the DOM-adsorbed fraction is completely unavailable. In contrast, $\alpha < 1$ implies that the DOM-adsorbed permethrin is partially bioavailable.

The measured C_{PDMS} data in **Figure 3** were used to fit eq 3, and good correlation was observed for all three DOM sources, with $r^2 = 0.90-0.95$. The measured BAF values in **Figure 2** were fitted to eq 4, and good correlation was also found for all three DOM sources, with $r^2 = 0.86-0.99$. Linear regression showed close correlation between permethrin BR in *D. magna* and C_{PDMS} when the data were plotted for each DOM source ($r^2 = 0.50-0.75$; $p < 0.0001$). Even when data from all three DOM sources were pooled, the linear correlation was still significant ($r^2 = 0.51$; $p < 0.0001$) with a slope of 0.34 ± 0.04 (**Figure 4**). The linear dependence validates that PDMS fibers acted as a biomimetic surrogate for permethrin in the test system and that PDMS accumulation may be used to predict the bioaccumulation potential of permethrin in DOM-containing water samples.

Regression of the measured C_{PDMS} and BAF data over [DOC] using eqs 3 and 4 yielded K_{DOC} and αK_{DOC} as regression parameters for each DOM source (**Table 2**). The K_{DOC} values estimated by PDMS fibers were consistently in the order of 10^4-10^5, suggesting high affinity of permethrin for aquatic DOM. Statistical comparison (paired *t* test) between K_{DOC} and αK_{DOC} derived from the BAF data showed that there was no significant difference between the two parameters at the 95% confidence interval regardless of the DOM source (**Table 2**). This observation suggests that the availability factor α was statistically 1 or that the DOM-adsorbed permethrin was completely unavailable for uptake by *D. magna* under the test conditions.

The effect of DOM on BAF was also influenced by DOM properties. Day (*9*) previously evaluated the effect of Aldrich humic acid on *D. magna* accumulation of several pyrethroids. The magnitude of reduction in BAF by DOM at comparable [DOC] levels was substantially greater for Aldrich humic acid

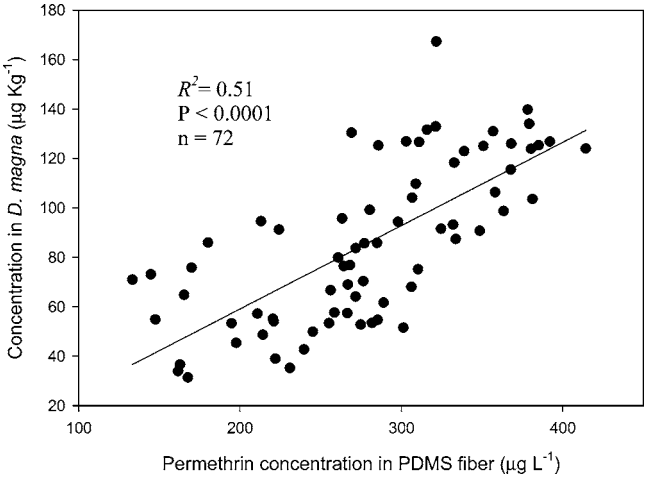

Figure 4. Correlation between permethrin body residues in *D. magna* and permethrin concentration in PDMS fibers exposed to the same samples containing DOM from three different sources.

Table 2. Regression Parameters K_{DOC} ($\times 10^4$) and αK_{DOC} ($\times 10^4$) Estimated for Permethrin Using Chemical-Based (PDMS) and Biological-Based (BAF and LC_{50}) Measurements in Dissolved Organic Matter-Containing Water Samples

	estimation method		
DOM source	PDMS	BAF	LC_{50}
lake water	4.74 ± 2.84	5.52 ± 0.89	3.4 ± 0.5
pond water	11.21 ± 1.38	9.51 ± 0.66	9.2 ± 0.7
compost extract	3.10 ± 0.69	4.69 ± 1.39	3.1 ± 0.3

than for the DOM sources used in this study. For instance, with [DOC] of 13.1 mg L^{-1}, Aldrich humic acid caused a reduction in *D. magna* uptake of deltamethrin and fenvalerate by 81−88%. At [DOC] of 15.5 mg L^{-1}, Aldrich humic acid decreased the acute toxicity of fenvalerate to *D. magna* by a factor of 17. In contrast, Hodge et al. (*10*) did not observe a significant effect of DOM of algal origin on the toxicity of fenvalerate on *D. magna* at low DOC levels (1.4−4.8 mg L^{-1}). The effect of DOM properties on bioavailability was previously demonstrated for other hydrophobic compounds (*23*, *24*), and the properties include aromaticity and content of certain functional groups. Due to the limited number of DOM sources used in this study, the role of DOM properties in affecting permethrin bioaccumulation was not further characterized and will be evaluated in future studies.

Effect of DOM on Acute Toxicity. The effect of DOM on another endpoint, acute toxicity, was evaluated using *C. dubia*. In DOM-free controls, the measured LC_{50} (0.48−0.56 μg L^{-1}) of permethrin was similar to the values reported by others (*8*). However, the LC_{50} of permethrin consistently increased, or the acute toxicity decreased, with increasing [DOC] in the test media (**Table 3**). Statistical analysis showed that the LC_{50} of permethrin was significantly ($\alpha = 0.05$) elevated in the pond water at [DOC] $\geq$ 5 mg L^{-1} and in the lake water and compost extract at [DOC] $\geq$ 10 mg L^{-1} (**Table 3**). Similar to the description for bioaccumulation, the effect of DOM on the acute toxicity may be expressed by eq 5

$$\mathrm{LC}_{50} = (1 + \alpha K_{\mathrm{DOC}}[\mathrm{DOC}]) \times \mathrm{LC}_{50(0)} \quad (5)$$

where $LC_{50(0)}$ is the LC_{50} value in the DOM-free control.

Good linear correlation was found for all DOM sources between the LC_{50} values and [DOC], with $r^2 = 0.92-0.98$ (p

Table 3. Influence of Dissolved Organic Carbon Level in Test Solutions on LC_{50} of Permethrin to *C. dubia*[a]

[DOC] (mg L^{-1})	LC_{50} (μg L^{-1}) lake water	LC_{50} (μg L^{-1}) compost extract	DOC (mg L^{-1})	LC_{50} (μg L^{-1}) pond water
0	0.52 (0.38–0.65)	0.48 (0.39–0.58)	0	0.56 (0.41–0.68)
1	0.57 (0.42–0.69)	0.52 (0.39–0.63)	0.5	0.51 (0.38–0.62)
5	0.54 (0.43–0.66)	0.49 (0.388–0.60)	1	0.59 (0.48–0.72)
10	0.74 (0.57–0.95)	0.59 (0.42–0.74)	2	0.66 (0.49–0.81)
20	0.78 (0.63–0.95)*	0.73 (0.52–0.90)*	5	0.76 (0.57–0.95)*
30	1.09 (0.81–1.39)*	0.92 (0.71–1.19)*	10	1.03 (0.81–1.32)*

[a] Values in parentheses are confidence intervals; * indicates statistically significant ($\alpha = 0.05$) increase over LC_{50} measured at [DOC] = 0.

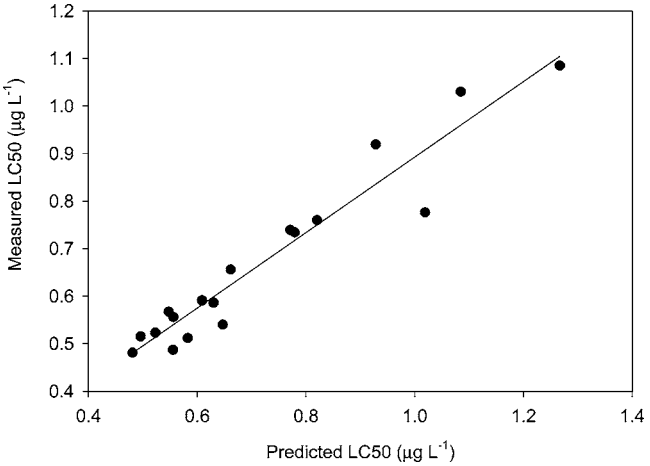

Figure 5. Correlation between measured LC_{50} and predicted LC_{50} of permethrin for *C. dubia* in water samples containing DOM from different sources and at different levels.

< 0.005). Even when data from all three DOM sources were pooled, the linear correlation was still statistically significant ($r^2 = 0.92$, $p < 0.0001$). This analysis suggests that DOM in water decreased the acute toxicity of permethrin and that the effect was consistent with the inhibitory effect on permethrin bioaccumulation by *D. magna* as well as enrichment on PDMS fibers. Regression of the measured LC_{50} using eq 5 yielded another set of αK_{DOC} for the three DOM sources (**Table 2**). Comparison between K_{DOC} and αK_{DOC} derived from LC_{50} revealed that the LC_{50}-based αK_{DOC} values were also statistically similar to K_{DOC} values for the same DOM source, again suggesting $\alpha \approx 1$, or that DOM-adsorbed permethrin did not contribute to the observed *C. dubia* toxicity in DOM-containing water samples and was therefore completely unavailable to the test organism.

Using the K_{DOC} values determined by PDMS fibers in **Table 2**, the LC_{50} for each [DOC] level was estimated from $LC_{50(0)}$. The predicted permethrin LC_{50} values were then plotted against the measured LC_{50} data in **Figure 5**. The estimated and measured values showed good linear correlation for permethrin ($r^2 = 0.92$) with slopes close to 1.0. This validates the feasibility of using PDMS fibers for predicting the actual permethrin toxicity for samples with known levels of [DOC].

In conclusion, owing to the strong adsorption of permethrin to aquatic DOM, the presence of DOM at naturally occurring levels significantly decreased the bioaccumulation and toxicity of permethrin to water-column invertebrates. The reduction in these endpoint effects was a result of the complete loss of bioavailability of the DOM-adsorbed permethrin. Results from this study clearly indicate that the role of DOM must be considered in understanding and regulating water quality risks imposed by pyrethroids. The decrease in bioavailability was predictable from changes in permethrin sorption to PDMS fibers for a given DOM source. However, the effect of DOM on the uptake and toxicity of permethrin appeared to depend also on the source of DOM. It will be therefore important to understand the dominant DOM properties that influence such interactions. In addition, as permethrin and other pyrethroids also have acute toxicity to benthic organisms that may have very different dietary behaviors from water-column invertebrates, it is imperative to also investigate the bioavailability and toxicity of pyrethroids to sediment-dwelling organisms.

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