Effects of Black Carbon on Pyrethroid Availability in Sediment

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Pyrethroids are widely used synthetic insecticides with the characteristics of high hydrophobicity and broad-spectrum aquatic toxicity. Many studies indicate that black carbon (BC) plays an important role in the bioavailability of hydrophobic compounds such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls in soils and sediments. However, the effect of BC on bioavailability of other compounds such as pyrethroids in sediments is less known. In this study, we simultaneously measured pyrethroid uptake into polydimethylsiloxane (PDMS) fibers and 24 h bioaccumulation in *Chironomus tentans* in a sediment amended with a charcoal at different rates. There were significant negative correlations between the accumulation of pyrethroids in PDMS fibers (C_{PDMS}) and the charcoal level in sediment. When the charcoal content was increased from 0 to 1.0%, C_{PDMS} decreased by 5.7–9.1%. Amendment of 1.5% charcoal to the original sediment decreased biota sediment accumulation factor (BSAF) of ^{14}C-permethrin in *C. tentans* from 2.8 to 1.7. The effect of charcoal was further found to be similar for the different subcellular fractions of *C. tentans*, including cell debris, organelles and proteins, and granules. The overall effect of charcoal on pyrethroid availability, however, was modest, and adsorption of pyrethroids on pure charcoal was found to be similar to that on sediment organic carbon. The relatively weak sorption on charcoal was likely due to the large molecular weight and sizes of pyrethroids, which might hinder their diffusion into charcoal nanopores.

KEYWORDS: Black carbon; bioavailability; pyrethroids; adsorption; sediment toxicity

INTRODUCTION

Synthetic pyrethroids are widely used pesticides for urban and agricultural insect control. Recent studies indicate that erosion and runoff can transport pyrethroids to surface water and sediments (*1–4*). For instance, in the San Diego Creek/ Newport Bay watershed located in Orange County, California, pyrethroids from <0.02 to 560 μg/kg were found in bed sediments (*4*). Pyrethroids are commonly toxic to aquatic organisms. For instance, the LC_{50} value of cypermethrin in sediments to *Chironomus tentans* is 13–62 μg/kg (*5*). Weston et al. (*6*) reported that pyrethroids, especially bifenthrin, were primarily responsible for the sediment toxicity to *Hyallela azteca* in the urban area of Roseville, California. Therefore, sediment toxicity due to pyrethroid contamination is a significant environmental concern, especially for regions where pyrethroids are widely used.

Natural carbonaceous materials, especially black carbon (BC), can protect organic pollutants from biological uptake or microbial degradation and subsequently decrease the ecological risk by adsorption (*7*). BC is produced from universal natural and anthropogenic processes, including the partial combustion of biomass and fossil fuels, and is composed of diverse types including char, charcoal, activated carbon, kerogen, and others (*7*). The total annual production of BC worldwide is 50–200 million tons, for which vegetation burning accounted for about 80% (*8*). It was further estimated that the environmental BC contributed about 80–90% of the total adsorption of soils and sediments for aromatic, planar, and hydrophobic compounds (*7–10*). Many bioaccumulation studies showed that the amendment of BC materials such as activated carbons significantly decreased the uptake of PAHs and PCBs from sediments (*11, 12*). However, most studies up to date have considered PAHs and PCBs, and relatively little is known about the effect of BC on other strongly hydrophobic organic compounds such as pyrethroid insecticides (*10, 14*).

Bioaccumulation is a direct approach to test chemical availability. For instance, a 28 day bioaccumulation study involving the clam *Corbicula fluminea* showed decreasing availability of PCBs from the sediment amended with activated carbon (*11*). However, the whole body burden may be a poor estimate of the effective concentration of chemicals inside the organism, because a chemical may have specific distribution patterns at the subcellular level. A recent study indicated that

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the differential toxicity of PAHs to *Capitella* species may be related to the subcellular distribution of PAHs inside the cell (*15*). Evidence also indicated that plant cells were able to sequester and reduce toxicity of organic contaminants by incorporation with cell wall materials and storage in vacuoles (*16, 17*). However, there is no knowledge on the subcellular fate of pyrethroids in benthic organisms.

The main objective of this study was to evaluate the impact of BC on bioavailability of pyrethroids in sediments. The chemical availability was measured by polydimethylsiloxane (PDMS) fibers using a method developed in previous studies (*18, 19*). In addition, distributions of pyrethroids in different subcellular fractions of *C. tentans* were studied using ^{14}C-permethrin as a model pyrethroid compound to understand if BC affected pyrethroid uptake and distribution at the subcellular level.

MATERIALS AND METHODS

Chemicals and Materials. Pyrethroids including bifenthrin (98.8%), fenpropathrin (99.7%), *λ*-cyhalothrin (98.7%), *cis*-permethrin (97.0%), *trans*-permethrin (97.0%), cyfluthrin (92.0%), cypermethrin (95.1%), and esfenvalerate (98%) were used in the PDMS fiber uptake experiment. These chemicals were obtained from FMC (Princeton, PA), Bayer CropScience (Stilwell, KS), Syngenta (Bracknell, Berks, United Kingdom), Valent (Walnut Creek, CA), or Chem Service (West Chester, PA). Carbon 14-labeled permethrin was used in the bioaccumulation experiment and subcellular fractionation analysis. The labeled permethrin (11.23 × 10^3 kBq/*μ*mol) was provided by FMC and purified using thin-layer chromatography plates before use. Tenax TA (60−80 mesh) was obtained from Supelco (Bellefonte, PA). All of the solvents and other chemicals used in the study were gas chromatography (GC) or analytical grade. PDMS fibers (430 *μ*m glass core with 35 *μ*m PDMS coating, Polymicro Technologies, Phoenix, AZ) were cut into pieces of 1 cm in length. Fibers were Soxhlet cleaned with ethyl acetate for 72 h before use.

A charcoal derived from coconut shell was used in this study as a BC material for amendment in the sediment (Agrocoir, Laguna Niguel, CA). Charcoal is one type of BC, and its adsorption capacity for hydrophobic compounds is around the median of various BC types (*7, 8*). Charcoal was crushed and sieved through a 2 mm mesh before use.

The sediment used in this study was collected from the top 10 cm at a location in San Diego Creek (Irvine, CA) and was wet sieved through a 2 mm mesh and stored at 5 °C before use. Detailed information about this sediment can be found elsewhere (*18*). The total organic carbon (OC) content of the sediment was 1.5%. The background BC content of the sediment was 0.03%, which was much lower than the lowest charcoal amendment rate (0.19%) used in this study. The BC content was determined according to the method of Gustafsson et al. (*9*). The dried and finely ground sediment was combusted in a muffle furnace at 375 °C for 24 h. Samples were then digested with HCl until effervescence ceased, and the BC content was then analyzed on a TOC analyzer.

Test Organisms. *C. tentans* (Aquatic Biosystems, Fort Collins, CO) was chosen for use in the bioaccumulation experiments because it is one of the indicator species recommended by the U.S. Environmental Protection Agency for sediment toxicity tests. The *C. tentans* was cultivated in the laboratory in reconstituted hard water (RHW) with silica sand as the substrate for several months at 22 ± 2 °C before use. The RHW contained NaHCO$_3$ (192 mg/L), CaSO$_4$·2H$_2$O (120 mg/L), MgSO$_4$ (120 mg/L), and KCl (8 mg/L). The photoperiod for organism stock cultures was 16:8 h light:dark. The *C. tentans* was fed a slurry of TetraFin Goldfish Flakes (Koi Lagoon, Fort Collins, CO).

Adsorption Experiment with Charcoal. A batch experiment was conducted to obtain the adsorption isotherms of pyrethroids on pure charcoal. Charcoal was spiked with pyrethroids at 1.0, 2.0, 5.0, 8.0, and 10.0 *μ*g/g by adding the pyrethroids in acetone to 0.1 g of charcoal in 20 mL scintillation vials and then 1.9 g of charcoal after the acetone evaporated dry overnight in a fume hood. After the spiked samples were mixed on a shaker at a high speed (around 200 rpm) for 4 h, 1.0 g (dry weight) of the charcoal, one piece of 1 cm PDMS fibers,

and 2.0 mL of deionized water with 200 mg/L NaN$_3$ were placed in 20 mL scintillation vials. The sample vials were rolled for 2 days at about 30 rpm, after which the fibers were retrieved and analyzed for the amount of pyrethroids accumulated (C_{PDMS}). PDMS fibers were removed and rinsed in deionized water, wiped with a paper towel, and then placed in 350 *μ*L glass inserts (Fisher Scientific, Pittsburgh, PA). Fibers were sonicated twice with 100 *μ*L of acetone for 5 min to extract the pesticides. The extracts were dried under a stream of nitrogen gas and redissolved in 100 *μ*L of hexane for analysis on GC using deltamethrin as the internal standard. The pyrethroid concentrations in PDMS fibers (C_{PDMS}) were analyzed on an Agilent 6890N GC equipped with an electron capture detector (Agilent Technologies, Wilmington, DE). The column used was an HP-5MS column (30 m × 0.25 mm × 0.25 *μ*m; Agilent Technologies). The oven temperature was initially held at 80 °C for 1.00 min, then ramped at 30 °C/min to 160 °C, followed by ramping at 3 °C/min to a final temperature of 300 °C that was held for 20 min. Method recoveries were 97 ± 17%. Decachlorobiphenyl was added to 20% of the samples as the surrogate, and the recovery for the surrogate was 81 ± 14%. The freely dissolved aqueous concentration C_w was estimated from C_{PDMS} and water partition coefficient K_{PDMS}. The K_{PDMS} values for all pyrethroids were obtained in a previous study except *λ*-cyhalothrin (*20*). The 2 day equilibration was demonstrated to be sufficiently long for pyrethroids to achieve equilibrium between sediment and water except for BF (*20*). Our previous work also indicated that the charcoal amendment did not change the desorption kinetics of pyrethroids from sediments (*21*).

The Freundlich model is widely used to describe the nonlinear adsorption isotherms for organic compounds on BC materials and in soils or sediments. The Freundlich model was used to describe adsorption to charcoal:

$$C_s = K_f C_w^n \tag{1}$$

where C_s is the adsorbed concentration on charcoal that is approximated by the spiked concentration due to the negligible partition of pyrethroids to water and fiber, K_f is the Freundlich adsorption coefficient for BC, and n is the Freundlich adsorption nonlinearity parameter.

Equilibration Experiment with PDMS Fibers. The sediment was spiked with 1.0 mg/kg of each pyrethroid. The pesticides in acetone were added to the bottom of a 1.9 L glass jar, followed by addition of 200 g of sediment after the acetone was evaporated dry in a fume hood and mixing thoroughly with a stainless steel spatula. After spiking, 30 g of spiked sediments was mixed with charcoal at amendment rates of 0, 0.19, 0.38, 0.57, 0.75, and 1.5% (dry weight basis) in 100 mL Teflon-lined glass jars. Pure charcoal was also similarly spiked with 5 mg/kg of each pyrethroid. Sodium azide solution (200 mg/L) was added to adjust the water content to 47% (w/w) to minimize microbial degradation during equilibration. The spiked sediments and pure charcoal in glass jars were shaken for 1 day at about 80 rpm on a horizontal shaker and then kept in the dark at room temperature. On 26 days after treatment, 1.0 g (dry weight) of sediment or charcoal was removed and transferred to 20 mL glass scintillation vials. For sediment and charcoal samples, respectively, 1.11 g and 0.87 mL of water with 200 mg/L NaN$_3$ was added to keep the water/sediment (or charcoal) ratio at 2:1. A 1 cm piece of PDMS fiber was added into the vials, and the samples were rolled (about 30 rpm) at room temperature for 48 h. Our previous studies showed that the uptake into PDMS fibers after 48 h of equilibration was able to mimic the bioavailable fraction of pyrethroids under agitated conditions (*18*). All treatments consisted of three replicates. The method for analyzing the uptake into PDMS fibers was the same as described above.

Bioaccumulation Experiment. ^{14}C-Permethrin was used to determine the subcellular distribution of pyrethroids because of the enhanced sensitivity of this technique as compared to the nonlabeled approach. The sediment was spiked with ^{14}C-permethrin at 0.1 mg/kg using the same procedure as described for the equilibrium experiment with the PDMS fiber. A 200 g aliquot of the spiked sediment was amended with charcoal at 0, 0.19, 0.38, 0.57, 0.75, and 1.5% in 1.9 L glass jars with lined metal caps. Samples in capped jars were shaken for 1 day at about 100 rpm on a horizontal shaker and then kept in the dark at room temperature to allow the spiked sediment samples to equilibrate.

Table 1. Adsorption Parameters of the Selected Pyrethroids on Charcoal Estimated Based on K_{PDMS} and Organic Carbon-Normalized Adsorption Coefficient (K_{oc}) from the Literature (23)[a]

compounds	Log K_f	n	r^2	median Log K_{BC}	Log K_{OC}
bifenthrin	5.88 ± 0.05	0.48 ± 0.10	0.98	5.32	5.73
fenpropathrin	5.89 ± 0.11	0.40 ± 0.13	0.92	5.10	5.07
cis-permethrin	5.89 ± 0.05	0.64 ± 0.03	0.99	4.84	5.66
trans-permethrin	5.70 ± 0.07	0.43 ± 0.06	0.97	4.72	5.61
cyfluthrin	5.00 ± 0.14	1.01 ± 0.08	0.88	5.01	5.87
cypermethrin	6.19 ± 0.19	0.99 ± 0.54	0.80	6.13	5.61
esfenvalerate	6.16 ± 0.19	0.86 ± 0.29	0.79	6.12	6.03

[a] K_f, adsorption coefficient based on the Freundlich model; *n*, nonlinear parameter.
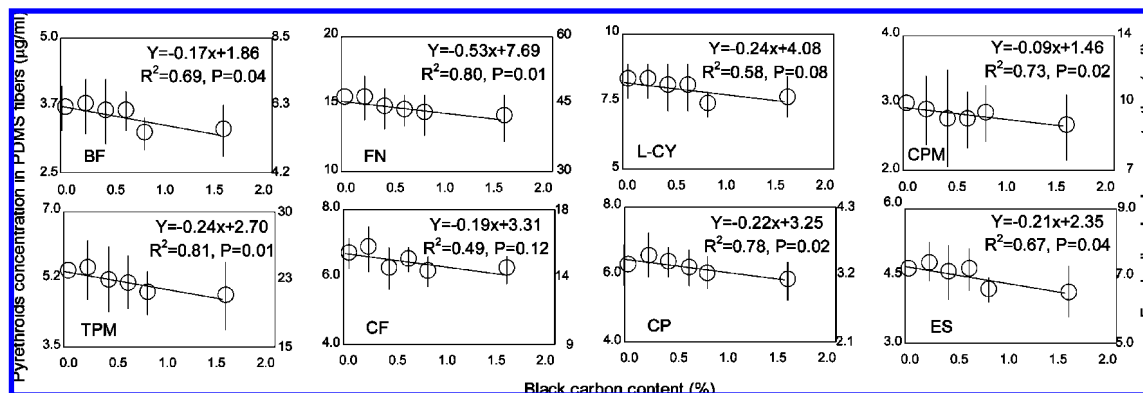
Figure 1. Correlations between concentrations of pyrethroids (ng) in PDMS fibers, freely dissolved concentrations, and amendment levels of charcoal (%) in sediment after 26 days of equilibration.

After 1 and 26 days of contact time, 15 g (dry weight) of sediment was removed with a stainless spatula and transferred to 100 mL glass jars followed by addition of 70 mL of RHW. After the sediment was settled overnight, 15 *C. tentans* (fourth-instar, based on head capsule width) were introduced into each test vessel.

Organisms were harvested after 24 h of exposure by filtering the sediment through a 1.0 mm sieve. Our previous studies showed that the uptake of permethrin into *C. tentans* reached equilibrium within 24 h (18). Ten *C. tentans* were rinsed in deionized water and placed on a piece of preweighed paper tissue (0.17 ± 0.03 g) to air-dry overnight. Dry organisms and paper were weighed again to obtain the dry weight of organisms. About 0.3 g (dry weight basis) of sediment was transferred onto an aluminum weighing dish (Fisher Scientific) and air-dried in a fume hood. Dry *C. tentans* and sediment samples were combusted at 900 °C for 2 and 4 min, respectively, on a R. J. Harvey OX-500 Biological Oxidizer (R. J. Harvey Instruments, Hillsdale, NJ), and the trapped $^{14}CO_2$ in 15 mL of carbon-14 cocktail (R. J. Harvey) was analyzed by liquid scintillation counting (LSC). Samples were counted for 6 min in triplicates. Recovery for the combustion method was 87−89%. Concentrations of ^{14}C-permethrin were calculated on the dry mass basis.

Five of the *C. tentans* harvested were used for the subcellular fractionation and analysis. The method for subcellular fractionation was similar to Wallace and Luoma (22). The dried *C. tentans* samples were weighed and then homogenized by sonication in 1.0 mL of 20 mM TRIS buffer (pH 7.6) for 5 min (Aldrich, St. Louis, MO). Homogenized tissues were centrifuged at 1450g (15 min, 4 °C). The supernatant represented organelles and proteins in *C. tentans*. The debris was then centrifuged in 1 M NaOH at 5000g for 10 min. Supernatant and debris after the centrifugation consisted of granules (metal-rich) and cellular debris, respectively. All subcellular fractions were mixed with 5 mL of C-14 cocktail in 7 mL scintillation vials and measured with LSC by counting samples for 6 min in triplicates. The mass balance for the subcellular experiment was 121.4 ± 5.3%, which showed that the subcellular protocol was relevant.

Statistical Analysis. Statistical analysis including a regression test and Pearson correlation test was performed using SPSS (SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Adsorption on Charcoal. Adsorption isotherms for the selected pyrethroids on charcoal were well-described by the Freundlich equation, and the estimated nonlinearity factor *n* ranged from 0.40 to 1.01 (**Table 1**). Given the nonlinear behavior for some of the pyrethroids, the value for the median adsorption coefficient (K_{BC}) was estimated for each pyrethroid and compared to K_{OC} values in the literature (**Table 1**) (23). It is evident that although adsorption of pyrethroids on charcoal was strong, K_{BC} values were similar to K_{OC} values for soils and sediments. In previous studies, pronounced increases in sorption due to BC amendment were observed for some compounds but not for the others. For instance, while K_{BC} measured for the herbicide diuron on wheat and rice charcoal was 400−2500-fold of K_{OC} (24), the effect of BC on sorption of atrazine was found to be negligible in another study (14). In addition, although the pyrethroids were spiked together, given the very low concentrations used, competition between adsorbates should be insignificant.

Effect of BC on Pyrethroid Availability in Sediments. Previous studies consistently showed that bioavailability of pyrethroids measured as bioaccumulation or toxicity was closely related to C_{PDMS} (18, 19). Therefore, accumulation into both PDMS fiber and *C. tentans* was determined in this study to quantify the influence of BC on the potential bioavailability of pyrethroids in sediments. Although the same amount was spiked for each pyrethroid in the same sediment, there were large differences in the detected C_{PDMS} values. After 26 days of incubation, C_{PDMS} was the highest for fenpropathrin (7.39 ± 0.31 ng) in the sediment with 0% BC and the lowest for *cis*-permethrin (1.41 ± 0.06 ng) in the sediment with 0.75% BC. Because NaN_3 was added to inhibit microbial degradation, these differences were apparently due to the different K_{PDMS} values associated with the individual pyrethroids, which likely reflected

Table 2. Comparisons of Experimental Conditions and Results between This and Earlier Studies on the Effect of BC on Availability of Hydrophobic Compounds

chemical	LogK_{ow}	MW[a]	planar	BC type	BC level (%)	availability decrease (%)	ref
pyrethroids	6.5–6.9	349–505	N	charcoal	1.50	8–12	
PAHs	3.4–6	128–252	Y	AC[b]	3.40	92	11
PAHs	3.4–6	128–252	Y	coke	3.40	38–64	11
PCBs	5.5–8	154–326	Y/N	AC	3.40	84	11
PCBs	5.5–8	154–326	Y/N	coke	3.40	<20	11
PCBs	5.5–8	154–326	Y/N	coal, AC	1.50	11–85	30
DDT	6.3	354	N	AC	3.20	83	31

[a] MW, molecular weight. [b] AC, activated carbon.
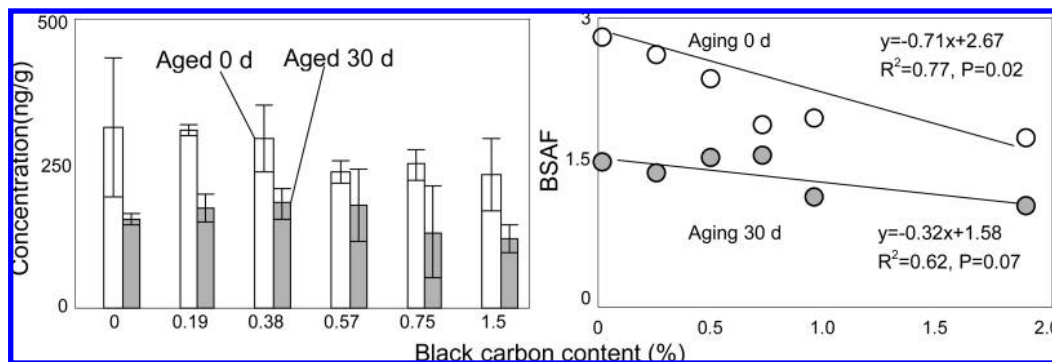
Figure 2. Concentrations and BSAF of pyrethroids in *C. tentans* from a sediment amended with a charcoal at different rates after fresh spiking and 30 days of equilibration.

different equilibrium partitioning between the sediment and the porewater phases for these compounds.

There was generally a significant negative correlation between C_{PDMS} and BC amendment rates (**Figure 1**). In the sediment with 1.5% BC, C_{PDMS} decreased by 12, 9, 8, 11, 12, 7, 8, and 10% for bifenthrin, fenpropathrin, λ-cyhalothrin, *cis*-permethrin, *trans*-permethrin, cyfluthrin, cypermethrin, and esfenvalerate, respectively, when compared with the sediment without BC amendment. The negative dependence of C_{PDMS} on the BC content was significant for all of the tested pyrethroids ($P <$ 0.05) except λ-cyhalothrin ($P = 0.08$) and cyfluthrin ($P = 0.12$). For a 1% increment in BC amendment rate, C_{PDMS} decreased by 5.7–9.1%.

The K_{BC} of phenanthrene for charcoal was found to be at the middle of K_{BC} values for a range of BC materials (8). However, there are no K_{BC} values available for pyrethroids on other types of BC. It is known that the background level of BC in natural sediments may consist of up to 50% of the total sediment organic carbon, which corresponds to the second highest amendment level in our study (25). Therefore, it may be concluded that the effect of BC on pyrethroids availability was modest, which was in contrast to the observation that 3% of BC amendment decreased the availability of PAHs and PCBs by up to 92% (11). However, this observation was in agreement with the fact that K_{BC} values of pyrethroids on charcoal were not much different from K_{OC} values as found in the above adsorption isotherm experiment. The relatively limited adsorption of pyrethroids on charcoal was also similar to that previously reported for atrazine (13, 14).

On the basis of the K_{PDMS} values of pyrethroids (20), C_w (freely dissolved concentration in pore water) was calculated from C_{PDMS}. After the sediments were equilibrated for 26 days, C_w was the highest for fenpropathrin (42.5–46.9 ng/L), while it was the lowest for cypermethrin (3.14–3.31 ng/L) (**Figure 1**). This difference may be attributed to the different chemical properties of pyrethroids. Most of the measured C_w values were far below the aqueous solubility limits of pyrethroids (26). In

You et al. (27), for sediments spiked with 1152 and 1434 ng/g permethrin, C_w was from 4 to 30 ng/L, which was similar to the values observed for *cis*-permethrin and *trans*-permethrin in this study. Previous studies showed that acute toxicity of pyrethroids to water-column invertebrate *Ceriodaphnia dubia* (28) and benthic invertebrate *C. tentans* (19), and uptake by water-column invertebrate *Daphnia magna* (29) and benthic invertebrate *C. tentans* (18), correlated significantly with C_w detected by PDMS fibers. Therefore, results from this study suggest that charcoal may have an influence on the bioavailability of sediment-borne pyrethroids similar to that of sediment OC.

The relatively small effect of BC on pyrethroid availability was inconsistent with previous findings for PAHs, PCBs, and DDT (**Table 2**). The factors contributing to the generally high sorption capacity of BC include adsorption on aromatic rigid surface sites and occlusion in nanopores (7). Adsorption of atrazine was found to correlate strongly with the content of aromatic carbons in BC sources (13). As compared with PAHs, the nonplanar structure of pyrethroids likely inhibited their adsorption to BC. For instance, Jonker et al. (30) demonstrated that the bioaccumulation of PCBs from sediments decreased with the molecular planarity. However, for nonplanar PCBs and DDT, 1.5–3.4% of BC amendment still decreased the availability by up to 85% (11, 30, 31). The adsorption of nonplanar diuron was 2 orders of magnitude stronger for BC than sediment OC (14). In another study, amendment of coke did not significantly decrease the availability of PCBs, but addition of activated carbon at the same level decreased PCBs availability by 84%, suggesting a strong influence by the type of BC materials (11). However, charcoal seemed to be an effective material for inhibiting the availability of PCBs, as 1.5% amendment decreased the availability by up to 85% (30).

A significant difference between pyrethroids and the other compounds in the cited studies is that pyrethroids have significantly higher molecular weights. The average molecular
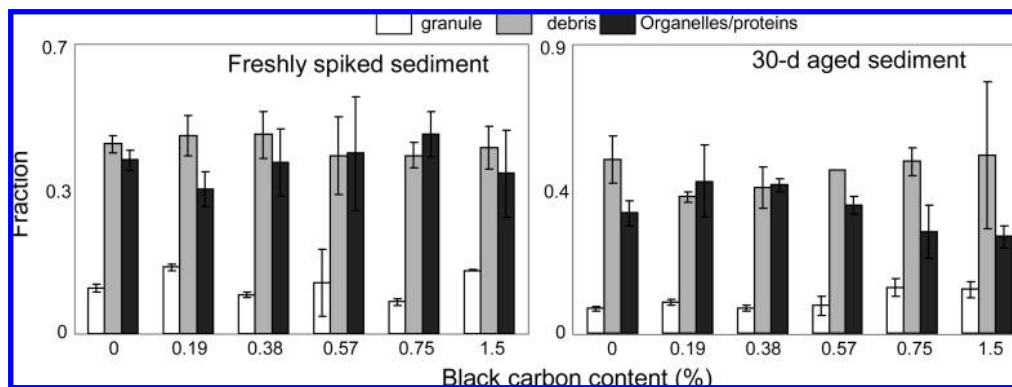
Figure 3. Fractions of ^{14}C-permethrin in cell granules, debris, and organelle/proteins of *C. tentans* exposed to freshly spiked and 30 days of incubated sediments.
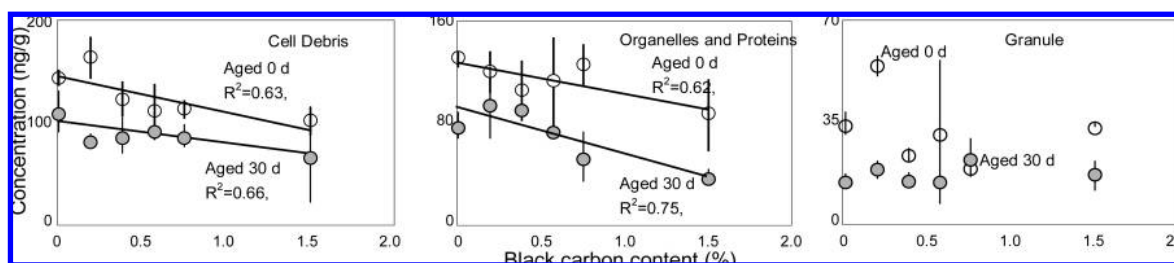

Figure 4. Concentrations of pyrethroids in cell granules, debris, and organelles/proteins of *C. tentans* exposed to sediments amended with charcoal at different rates.

weight of pyrethroids is about 250 g/mol greater than that of PAHs and about 200 g/mol greater than that of PCBs. The higher molecular weight may decrease the rate at which the pyrethroid molecules diffused into the nanopores (*32, 33*). Using ChemOffice2004 (Cambridgesoft, Cambridge, MA) and Gaussian 03W (Wallingford, CT), we calculated the molar volumes of the test pyrethroids to be 211.6−263.2 cm^3, which are considerably larger than DDT (181.1 cm^3), phenanthrene (115.4 cm^3), and most PCBs (143.6−229.7 cm^3). Nguyen et al. (*33*) found that the maximum sorption on chars (another kind of BC material) for hydrophobic chemicals decreased with increasing molecular diameters, suggesting the importance of molecular size in adsorption on BC. In a study on partition of PCBs into a polymer film, Yang et al. (*32*) showed that diffusion of higher molecular weight PCBs was inhibited by their larger sizes. Therefore, the large molecular sizes probably led to the reduced diffusion of pyrethroids into the nanopores of charcoal and hence the adsorption on inner surfaces.

Accumulation into *C. tentans*. ^{14}C-Permethrin concentrations in *C. tentans* cultured in freshly spiked sediments ranged from 231 to 312 ng/g (based on whole body dry weight). The measured ^{14}C-permethrin likely included some metabolites; however, our previous study indicated that the accumulation achieved a steady state within 24 h of exposure (*20*). When cultured in the amended sediments that were equilibrated for 26 days, permethrin concentrations in whole organisms decreased to 120−180 ng/g, suggesting that aging or degradation had an effect on permethrin accumulation by *C. tentans* (**Figure 2**). Biota-sediment accumulation factor (BSAF) calculated as the ratio of pesticide concentration in *C. tentans* to that in the sediment ranged from 1.10 to 2.84 (**Figure 2**). Maund et al. (*5*) showed that the BSAFs of cypermethrin in sediment with 1−13% organic carbon for *C. tentans* were 0.08−0.63, which was smaller than what was observed in this study. This may be attributed to

differences in sediment OC contents. BSAFs decreased by 20−27% as the BC content was increased from 0 to 1.0%. The response of BSAF to BC content was therefore more pronounced than the decreasing trend for C_{PDMS}. However, the effect of BC amendment on BSAF for pyrethroids was also substantially less than those observed for the other chemicals. For instance, McLeod et al. (*34*) observed that 0.7, 1.3, and 2.5% of activated carbon amendment decreased the accumulation of PCBs into the clam *Corbicula fluminea* by 67, 86, and 95%. Biodynamic modeling showed that mass transfer from sediment particles to activated carbon and reductions in aqueous concentrations both contributed to the decreased bioaccumulation (*34*).

Subcellular distribution is a potentially important factor in the fate and toxic effects of organic pollutants (*15, 35*). Analysis of ^{14}C activity in different subcellular fractions of *C. tentans* showed that on the average about 12, 46, and 42% of ^{14}C-permethrin was associated with granules, cell debris, and organelle/proteins, respectively (**Figure 3**). The preferential accumulation of permethrin in cell debris and organelle/proteins suggests a selective association of permethrin with these subcellular phases. Bach et al. (*15*) observed that *Capitella* sp. S was more sensitive to fluoranthene than *Capitella* sp. I, although *Capitella* sp. I accumulated significantly more fluoranthene than sp. S in the cytosol fraction that contained a large number of enzymes and proteins. The researchers concluded that the proteins including a large number of enzymes were important for the detoxification of fluoranthene in *Capitella*. In another study, results obtained using two-photon excitation microscopy techniques showed that vacuoles in spinach, as the "toxic waste dump", accumulated most of phenanthrene together with a large number of proteins (*35*). Other studies suggested that specific proteins (transporters) inhibited the accumulation of toxicants and protect the organism from toxic effects (*36, 37*). Cornwall

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et al. (*38*) demonstrated that the accumulation of pesticide dimethyl tetrachloroterephthalate in mussel gills was inhibited by specific proteins (i.e., efflux transporters).

The distribution of ^{14}C-permethrin among the three subcellular fractions did not appear to be affected by the charcoal amendment. As the charcoal amendment rate was increased, the concentrations of ^{14}C-permethrin in cell debris and proteins/organelles decreased proportionally ($P = 0.05$ and 0.06, respectively), although a weaker relationship was found for granules ($P = 0.84$) (**Figure 4**). BSAFs were further calculated for the different subcellular fractions. BSAFs for cell debris, organelles, and proteins showed significant negative correlations with the BC content in the sediment. These results suggested that association of permethrin with proteins and organelles, likely an important process for detoxification, decreased proportionally along with the effect of BC on the total body residue as well as C_w.

Results from this study provided evidence that while there were significant negative correlations between availability of pyrethroids and BC content, the influence of BC such as charcoal was rather limited and was similar to that of sediment OC. The limited effect of BC on pyrethroid availability may be due to the large molecular size of pyrethroids, which hindered diffusion or sorption. Amendment of BC showed a uniform effect on the distribution of ^{14}C-permethrin in different subcellular fractions of *C. tentans*, including the fraction associated with proteins/organelles that are likely linked to detoxification.

ACKNOWLEDGMENT

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