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Ecological bioavailability of permethrin and *p,p′*-DDT: Toxicity depends on type of organic matter resource

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HIGHLIGHTS

- Greater adsorption of permethrin and *p,p′*-DDT for sediment than leaf material.
- Lower OC-based toxicity to *H. azteca* when sediment present with leaf material.
- Toxicity of insecticides to *H. azteca* depends on type of organic matter resource.
- Organisms' habitat composition must be considered to assess risk of contaminants.

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ABSTRACT

Hydrophobic organic contaminants readily partition from aqueous to organic phases in aquatic systems with past research largely focusing on sediment. However, within many aquatic systems, matrices such as leaf material and detritus are abundant and ecologically important, as they may represent a primary exposure route for aquatic invertebrates. The objectives of the present study were to examine partitioning and toxicity to *Hyalella azteca* among permethrin and *p,p′*-DDT contaminated sediment, leaf, and a sediment-leaf mixture. Log organic carbon–water partitioning coefficients ranged from 4.21 to 5.82 for both insecticides, and were greatest within sediment and lowest in coarse leaf material. *H. azteca* lethal concentrations for 50% of the population (LC50s) ranged from 0.5 to 111 μg g^{-1} organic carbon, and were dependent on the matrix composition. The variation in sorption and toxicity among matrices common within stream ecosystems suggests that the ecological niche of aquatic organisms may be important for estimating risk of hydrophobic pesticides.

1. Introduction

In aquatic ecosystems, allochthonous leaf litter inputs are a primary source of organic material into stream ecosystems, providing a linkage of terrestrial and aquatic systems (Wallace et al., 1997), and a major food and habitat resource for benthic invertebrate communities (Webster et al., 2001). The organic matter sources (e.g., coarse versus finer particulate organic matter) and the degree to which these materials are utilized vary based upon the feeding group (e.g., shredders, collector-gatherers, collector-filterers) the organism belongs to within the system (Cummins and Klug, 1979; Wallace and Merritt, 1980; Sinsabaugh et al., 1985; Arsuffi and Suberkropp, 1986, 1989; Harris, 1993; Hall and Meyer, 1998).

In addition to being important for cycling of organic carbon and critical for stream ecosystem functioning (Vannote et al., 1980; Wallace et al., 1997), allochthonous carbon-based inputs also represent a major adsorptive substrate for hydrophobic organic contaminants. Differences in binding affinity between the surfaces of sediment and leaf material may result in substantial differences in partitioning of hydrophobic contaminants, pore water concentrations, bioavailability, and ultimately toxicity to benthic invertebrates. However, to date, few researchers have attempted to characterize the partitioning properties of these compounds in mixed-matrix systems. Studies usually focus solely on sediment-associated toxicity (Weston et al., 2005, 2006; Amweg et al., 2006, 2009; Ng et al., 2008; Trimble et al., 2009), and toxicity of leaf-associated insecticides to benthic invertebrates remains largely unknown. One such study by Maul et al. (2008) examined the partitioning and matrix-specific toxicity of the pyrethroid insecticide bifenthrin in sediment, detritus, and leaf material. Another study by Moore et al. (2007) presented toxic effects of the pyrethroid insecticides lambda-cyhalothrin and cyfluthrin in water, leaf litter and sediment phases in a constructed wetland to *Hyalella azteca*. Other frequently detected pyrethroid

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insecticides have yet to be studied in this respect. Also, despite the continued detections of legacy organochlorines in the environment, little attention has been given to determining how compounds, such as *p,p′*-DDT, partition between sediment and leaf-material common to most aquatic ecosystems.

The first objective of the present study was to examine variation in partitioning of the pyrethroid insecticide permethrin and organochlorine insecticide *p,p′*-DDT among two sediments of varying characteristics and three particulate size fractions of leaf material that vary in their function as a resource for invertebrates (Cummins and Klug, 1979). The second objective was to examine variation in toxicity of permethrin and *p,p′*-DDT to a shredding benthic invertebrate (*H. azteca*) when the insecticides were sorbed to different matrices containing organic carbon (OC) (i.e., sediment, leaf material, and a mixture of both).

2. Materials and methods

2.1. Chemicals

Analytical grade permethrin [cyclopropanecarboxylic acid, 3-(2,2-dichloroethenyl)-2,2-dimethyl-(3-phenoxyphenyl)methyl ester] and *p,p′*-DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane] were purchased from Chem Service Inc. (West Chester, PA, USA). Neat chemical purities were 98% (47.6% cis-isomer and 50.4% trans-isomer) for permethrin and 99.5% for *p,p′*-DDT. Radiolabeled [^{14}C] permethrin and [^{14}C] *p,p′*-DDT solutions were obtained from Sigma–Aldrich Company (St. Louis, MO, USA). The specific activities of the primary stock solutions were 10.9 and 12.8 μCi μmol^{-1} for [^{14}C] permethrin and [^{14}C] *p,p′*-DDT, respectively. The purities of all radiolabeled stock solutions were found to be >97%, using an Agilent 1100 Series High Performance Liquid Chromatography (HPLC) (Agilent Technologies, Palo Alto, CA, USA) and a Packard 1900TR liquid scintillation counter (LSC) (Packard Instrument Company, Downers Grove, IL, USA). Pesticide and HPLC grade solvents used in all experiments were obtained from Fisher Scientific (Pittsburgh, PA, USA).

2.2. Sediment, leaf, and detrital matrices

Reference sediment was collected at the Touch of Nature Field Station located 15 km south of Carbondale, IL, USA and sieved to ⩽500 μm with a No. 35 US standard sieve. Organic carbon content of this sediment was 0.69 ± 0.10% (n = 3), it was classified as silt loam with 14%, 70%, and 16% sand, silt, and clay, respectively, and had a cation exchange capacity (CEC) of 5.7 mEq/100 g (Mid-West Laboratory, Omaha, NE, USA). This sediment was used for the partitioning experiments in the present study and represented low OC sediment referred to as Sed-LOC. A second collection was made from the same location to obtain additional sediment for use in all toxicity studies. This sediment was also classified as silt loam with 14%, 72%, and 14% sand, silt, and clay, respectively. The OC content was 0.98 ± 0.10% (n = 3) and CEC was 10.0 mEq/100 g. The high OC sediment used in the partitioning experiments was collected from West Bearskin Lake in Cook County, MN, USA (Leonard et al., 1999; Norberg-King et al., 2006). It was classified as sandy clay loam with 55%, 12%, and 33% sand, silt, and clay, respectively. The OC content was 7.85 ± 0.18% (n = 3) and CEC was 14.0 mEq/100 g. This high-OC sediment will be referred to as Sed-HOC.

Senesced sugar maple leaves (*Acer saccharum*) were collected from the Touch of Nature Field Station within 7-d of abscission and prior to any rain events that may have caused leaching. Sugar maple leaves were used because they represent a labile organic matter food resource frequently used by amphipods (Macneil et al., 1997). Dried leaves were soaked in dechlorinated water for 7-d prior to placing them into *H. azteca* culture tanks to remove any excess water-soluble compounds that may have been detrimental to the health of culture organisms. Freshly soaked leaf material was added as necessary beginning at least one year prior to these experiments to allow for an adequate amount of processed material to be available.

Three different leaf fractions, free from any *H. azteca*, were collected from these culture tanks and included coarse particulate organic matter (CPOM) (particle size between 2000 and 1000 μm), fine particulate organic matter (FPOM) (particle size between 1000 and 212 μm), and very fine particulate organic matter (VFPOM) (particle size between 212 and 8 μm) following the methods of Maul et al. (2008). Total organic carbon content was 42.60 ± 0.07%, 40.00 ± 0.07%, and 39.20 ± 0.64% for CPOM, FPOM, and VFPOM, respectively.

2.3. Partitioning of compounds among sediment and detrital matrices

Partitioning of permethrin and *p,p′*-DDT was examined among the two sediments (Sed-LOC and Sed-HOC) and the three organic matter fractions (CPOM, FPOM, and VFPOM). For both chemicals, 10 mg (dry mass) of each matrix was added to separate 20 mL scintillation vials in triplicate. Twelve mL of aqueous [^{14}C] permethrin or [^{14}C] *p,p′*-DDT solution with a concentration of 30 μg L^{-1} was added to each vial, capped, and rotated using a wheel rotator (1245 inversions h^{-1}). All aqueous chemical solutions were prepared using moderately hard reconstituted water (MHRW). Partitioning of each of the chemicals was determined at four different time points: 0.25, 6, 48, and 96-h, and [^{14}C] permethrin and [^{14}C] *p,p′*-DDT concentrations were determined using LSC with correction for background radiation and quenching.

Sorption coefficients, K_d, were calculated for each compound by dividing the concentration in the solid matrix (μg chemical g^{-1} of pellet dry weight) by that in the aqueous phase (μg chemical mL^{-1} of supernatant) for each of the five matrices, after equilibrium was reached. Organic carbon normalized sorption coefficients, K_{oc}, were then calculated by dividing K_d by the OC content of each matrix. Variation in the sorption coefficients, K_d and K_{oc}, was examined among each of the five matrices using one-way ANOVA and Tukey–Kramer multiple comparisons (JMP version 8.0.2).

2.4. Toxicity of permethrin and p,p′-DDT to H. azteca in sediment and leaf

Toxicity of permethrin and *p,p′*-DDT to *H. azteca* was determined for three separate matrix treatments: sediment (i.e., Sed-LOC described previously), whole sugar maple leaf material, and an equal organic carbon mixture of the two. For the sediment treatment, 40.00 ± 0.01 g (mean ± s.d.) of dry sediment were added to individual 200 mL glass jars. Similarly, for the leaf treatment, 874.5 ± 0.2 mg of dry maple leaf was added to a second set of jars. For the mixture, 20.00 ± 0.01 g of dry sediment and 437.3 ± 0.3 mg of dry leaf material was added to a third set of jars. This resulted in approximately 393.2 mg of OC in each experimental unit. Once the sediment and leaf material were weighed into the jars, 100 mL of MHRW was added to each. Jars were then allowed to sit for 7-d at 4 °C in the dark to ensure that all leaf material was thoroughly saturated. Next, 50% of the overlying water was removed from each leaf and mixture jar and replaced with fresh water prior to spiking with pesticide stock solutions. Total compound concentrations and [^{14}C] concentrations of stock solutions were verified via HPLC and LSC, respectively, and were within 5% of nominal concentrations. Each matrix treatment consisted of seven concentrations with three replicates per concentration. In addition, control beakers