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Using SPME fibers and Tenax to predict the bioavailability of pyrethroids and chlorpyrifos in field sediments

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ABSTRACT

The presence of pyrethroids in both urban and agricultural sediments at levels lethal to invertebrates has been well documented. However, variations in bioavailability among sediments make accurate predictions of toxicity based on whole sediment concentrations difficult. A proposed solution to this problem is the use of bioavailability-based estimates, such as solid phase microextraction (SPME) fibers and Tenax beads. This study compared three methods to assess the bioavailability and ultimately toxicity of pyrethroid pesticides including field-deployed SPME fibers, laboratory-exposed SPME fibers, and a 24-h Tenax extraction. The objective of the current study was to compare the ability of these methods to quantify the bioavailable fraction of pyrethroids in contaminated field sediments that were toxic to benthic invertebrates. In general, Tenax proved a more sensitive method than SPME fibers and a correlation between Tenax extractable concentrations and mortality was observed.

1. Introduction

Pyrethroid insecticides have been detected in sediment and water samples at concentrations lethal to invertebrates throughout the United States (Weston et al., 2004, 2005, 2009a,b; Weston and Amweg, 2007; Weston and Lydy, 2010; Holmes et al., 2008; Hintzen et al., 2009; Ding et al., 2010; Kuivila et al., 2012). Therefore, it is important to have an accurate and effective means of assessing the potential impact of these pesticides in the environment. The difficulty in making such assessments is the same as with other hydrophobic organics; assessing bioavailability in these complex matrices is challenging. A proposed solution to this problem was the use of bioavailability-based chemical techniques (Mayer et al., 2000; Cornelissen et al., 2001). These methods take bioavailability into consideration; therefore, providing more accurate measures of potential bioaccumulation and toxicity. While the majority of studies have used these techniques to assess bioaccumulation, there has been an increasing focus on their utilization in toxicity estimates (Xu et al., 2007; Harwood et al., 2012a).

Two commonly used bioavailability-based techniques are solid phase microextraction (SPME) fibers and Tenax beads. The SPME fiber can be used to make estimates of chemical activity (Mayer et al., 2000) and Tenax beads measure desorption potential from the sediments (Cornelissen et al., 2001). Therefore, the concentrations measured by the two techniques are proportional to the chemical activity and bioaccessible fractions, respectively (Semple et al., 2004). There are potential strengths and limitations of each method. The SPME fiber may be used in the field which may better represent exposure; however, it requires equilibrium conditions, which may take several weeks to months to achieve. Further, techniques must be established to use the fibers in a range of sediment conditions including differing depths of water and sediment compositions. In addition, in order to reach equilibrium, the fibers must not deplete the chemical concentration in the system as this would shift equilibrium (Mayer et al., 2000). However, there are non-equilibrium based SPME methods. Tenax extraction does not have the depletion or equilibrium requirements, which is an advantage. Typically, a single 6- or 24-h Tenax extractable concentration has been correlated to bioaccumulation or toxicity (You et al., 2008, 2011), making it a faster technique and one that has greater sensitivity. The Tenax method, however, cannot be used *in situ*. Both methods have been used to successfully assess the bioavailability of hydrophobic organics in laboratory-spiked and in field-contaminated sediments (reviewed in You et al., 2011) and studies have compared the applicability of these methods directly using field sediments for compounds such as PCBs (Landrum et al., 2007; Trimble et al., 2008; You et al., 2007). Limited research, however, has been conducted using these methods for relatively toxic hydrophobic organics, such as pyrethroid insecticides. The objective of the current study was to compare the potential of the two techniques to

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estimate the toxicity of pyrethroid insecticides in contaminated sediments. Specifically, the ability of these methods to measure environmentally and toxicologically relevant concentrations in pyrethroid and chlorpyrifos contaminated field sediment was evaluated. Chlorpyrifos was also included as it is often detected with pyrethroids in agriculture-influenced sediments (Ding et al., 2010).

2. Materials and methods

2.1. Chemicals

Sediments, SPME fibers, and Tenax extracts were analyzed for nine pyrethroid insecticides (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, λ-cyhalothrin, permethrin, and tefluthrin) and an organophosphate pesticide (chlorpyrifos). These pesticides were purchased as a custom standard mix from Accustandard (New Haven, CT, USA). The two surrogates, 4, 4′-dibromooctafluoro-biphenyl (DBOFB) and decachlorobiphenyl (DCBP), were obtained from Supelco (Bellefonte, PA, USA). The purity of all the standard chemicals was ≥97% as indicated by the manufacturer. Acetone, dichloromethane, and hexane (all pesticide grade); along with silica and copper were purchased from Fisher Scientific (Pittsburg, PA, USA). Dual layer ENVI-CarbII/polymerically bonded ethylenediamine-N-propyl (PSA) solid phase extraction cartridges were purchased from Supelco (Bellefonte, PA, USA). The SPME fibers had a 10 μm polydimethylsiloxane (PDMS) coating for a phase volume of 0.069 μL per cm of fiber (Fiberguide Industries, Stirling, NJ, USA). Laboratory-exposed fibers were held in 105 μm stainless steel mesh screen packets to protect them from damage during the laboratory exposure and previous studies have shown no effect of the screens on fiber exposure (You et al., 2006). In the field-deployed SPMEs, a 110 μm copper screen was used to prevent biofouling.

2.2. Sediment collection

Sediments were collected at six sites with expected pyrethroid contamination in northern California in April 2011 (Table S1). Four of these sites were from urban landscapes and included Grayson Creek (Concord, CA), Mosher Slough (Stockton, CA), Curry Creek (Roseville, CA), and Strong Ranch Slough (Sacramento, CA). The remaining sites, Del Puerto and Ingram Creeks near Modesto, CA, primarily had agricultural input. At each site, the surface sediment (less than 2 cm deep) was gently removed using a clean stainless steel scoop and placed in two clean 4 L glass jars. Jars were stored on ice until they were returned to the University of California Berkeley where they were stored at 4 °C. After all the sediments had been collected they were shipped to Southern Illinois University-Carbondale (SIUC) where they were also stored at 4 °C until use (less than 7 d post sampling).

2.3. Toxicity bioassays

Sediments were warmed to room temperature, homogenized, and all large debris were removed manually. Toxicity tests were conducted using three species: 7–10 d old *Hyalella azteca*, 3rd instar *Chironomus dilutus*, and 10 mm *Hexagenia* sp. nymphs. Four replicates were used for each sediment and species for a total of 72 replicates. Reference sediment free of detectable analytes (Bay Creek, Pope County, IL, 1.42 ± 0.05% organic carbon) was used as a negative control. Animals were taken from cultures at SIUC. *Hyalella* and *Chironomus* were cultured according to standard US EPA protocols (US EPA, 2000) and *Hexagenia* were cultured according to established SIUC methods (Harwood et al., 2012b). After 10 d, exposed animals were sieved from the sediments and living animals were enumerated. Additional method details are available in Supporting information. Toxicity was considered significant if it was significantly greater than control mortality (Dunnett's multiple comparison test).

To confirm pyrethroids as a potential source of toxicity, the toxic units were calculated for *H. azteca* by taking sediment pyrethroid concentrations and dividing by literature median lethal concentrations (Maund et al., 2002; Amweg et al., 2005).

2.4. Sediment extractions

Sediments were extracted using methods described in Ding et al. (2010). Additional details are available in Supporting information.

2.5. SPME fibers

For field deployment, 15 cm of PDMS coated disposable SPME fibers were placed in a square Plexiglas holder with an open center containing a 110 μm mesh copper screen. Fibers were placed within the copper screen in order to maintain contact with the interstitial water, while protecting the fiber. Copper was used to discourage the formation of biofilms on the fibers. The *in situ* devices were strapped to a square cement paving stone approximately 10 cm apart using plastic zip ties. Each stone contained six devices (Fig. S1). The stones were placed on the sediment surface, the devices were set 15 cm away from the stone, and the SPMEs were gently buried in the first few cm of sediment (Fig. S1). The devices remained in the field for 42 d to ensure equilibrium (Harwood et al., 2012b). Two devices were pooled per replicate for a total of three replicates per site. The devices were returned to the laboratory, rinsed with moderately hard water (MHW), and the fibers were removed. If fibers were dirty, they were placed on a clean moist paper towel and gently rolled to remove any debris. Previous preliminary testing in our laboratory has demonstrated this process does not influence fiber concentrations. Surrogates (DBOFB and DCBP) were added prior to shipping and a spike check was shipped with all samples. Fibers were stored in hexane and shipped on ice to SIUC.

In the laboratory experiments, approximately 15 g wet sediment was added to four replicate 20 ml scintillation vials. A set of Bay Creek control replicates were also prepared. To each vial, four stainless steel packets containing 10 cm of fiber were added. Three ml of a 3 mg/ml solution of mercuric chloride was added to each vial to prevent microbial degradation and the vials were filled with MHW. Vials were then gently shaken at 100 revolutions per minute for 42 d. At the conclusion of the exposure, fibers were removed from the sediments, rinsed with MHW and placed in hexane and surrogates were added. All fibers were extracted in 1 ml of hexane per 10 cm of fiber by storing the fibers in hexane a minimum of 36 h at 4 °C. The hexane was then solvent exchanged to 100 μl of acetified hexane.

2.6. Tenax extractions

The 24 h single-point Tenax extractions were conducted as described in You et al. (2008). Briefly, 2 g of sediment (dry weight) was distributed into four replicate 50 ml test tubes per sediment. Tubes were rotated for 24 h, after which the tubes were centrifuged; Tenax was removed, placed in a 20 ml vial and extracted as described in Supporting information.

2.7. Quality assurance and quantification

Quality assurance and quality control for sediment extractions consisted of a laboratory control blank, matrix spike, and matrix spike duplicate. The laboratory control blank consisted of sea sand spiked with surrogates only and the matrix spikes were control sediment spiked with surrogates and the analytes of interest in an acetone carrier. For SPME fibers and Tenax extractions, control samples were extracted as matrix blanks and these extracts only contained surrogates. Chemical analysis of extracts were performed using an Agilent 6890 series gas chromatograph (Agilent Technologies) with a microelectron capture detector as detailed in Ding et al. (2010). Quantification and quality assurance procedures are described in more detail in Supporting information.

3. Results and discussion

3.1. Quality control

Control survival of the test species exposed in Bay Creek sediment in all experiments was 97 ± 5%, 83 ± 5%, and 100% for *H. azteca*, *C. dilutus*, and *Hexagenia* sp., respectively. Water quality parameters remained within US EPA (2000) acceptable limits (temperature 23 ± 0.1 °C, conductivity 377 ± 29 μS/cm, dissolved oxygen 7.42 ± 1.21 mg/L, pH 6.71 ± 0.18). Pyrethroid and chlorpyrifos concentrations on the control SPMEs and Tenax were below reporting limits.

3.2. Pyrethroid and chlorpyrifos sediment concentrations and observed toxicity

The field-collected sediments contained detectable levels of pyrethroids, with five of the nine pyrethroids and chlorpyrifos being found in at least one sediment (Table S1). This observation was expected as these were sites where pyrethroids had been previously detected. Previous studies have implicated pyrethroids as the source of toxicity to *H. azteca* in Curry Creek (Amweg et al., 2006), Strong Ranch Slough (Amweg and Weston, 2007; Weston et al., 2006), Del Puerto Creek (Weston and Amweg, 2007; Weston et al., 2008), and Ingram Creek (Weston et al., 2004; Domagalski et al., 2010), using either toxicity identification evaluations (Strong Ranch Slough and Del Puerto Creek) or sediment concentrations related to known toxicity thresholds (Curry and Ingram Creeks). The role of pyrethroids in toxicity at these sites was further supported by calculating *H. azteca* toxic units (Table 1). Toxic units are only presented for *H. azteca* because literature LC50 values were available for all detected analytes for only this species,