Copper clean-up procedure for ultrasonic extraction and analysis of pyrethroid and phenylpyrazole pesticides in sediments by gas chromatography-electron capture detection

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ABSTRACT

A rapid ultrasonic extraction method coupled with a heated-copper clean-up procedure for removing interfering constituents was developed for analyzing pyrethroid and phenylpyrazole pesticides in sediments. Incubation of the 60 mL extract with 12 g copper granules at 60 °C for 2 h was determined to be the optimal conditions for removing the interfering constituents. Eleven pyrethroid and phenylpyrazole pesticides were spiked into sediment samples to determine the effectiveness of the ultrasonic extraction method. The average recoveries of pyrethroids and phenylpyrazoles in sediment at 4 °C storage on day 0, 1, 7, 14, and 21 ranged from 98.6 to 120.0%, 79.2 to 116.0%, 85.0 to 119.7%, 93.6 to 118.7%, and 92.1 to 118.2%, respectively, with all percent relative standard deviations less than 10% (most <6%). This illustrated the stability of pyrethroids and phenylpyrazoles in sediment during sediment aging at 4 °C. Recoveries of the pesticides ranged from 98.6% to 120.0% for lowest fortification level (2–16 μg kg^{-1}), from 97.8% to 117.9% for middle fortification level (10–80 μg kg^{-1}), and from 94.3% to 118.1% for highest fortification level (20–160 μg kg^{-1}). Relative standard deviations of pesticide recoveries were usually less than 7%. Method detection limits of target pesticides ranged from 0.22 μg kg^{-1} to 3.72 μg kg^{-1}. Furthermore, field sediment samples collected from four residential lakes during a three-month monitoring period were analyzed to evaluate the effectiveness of this method. Bifenthrin was detected in all of sediment samples (highest concentration 260.33 ± 41.71 μg kg^{-1}, lowest concentration 5.68 ± 0.38 μg kg^{-1}), and fipronil sulfone was detected at least once in sediment samples collected from three sites with concentrations ranging from 1.73 ± 0.53 to 7.53 ± 0.01 μg kg^{-1}.

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1. Introduction

Possessing advantages of lower mammalian toxicity, selective insecticidal activity, and lower environmental persistence, pyrethroid and phenylpyrazole pesticides have increasingly replaced organophosphate, organonitrogen, and organochlorine pesticides which are more toxic and tend to accumulate in living organisms (Hainzl et al., 1998; Mize et al., 2008; Vidau et al., 2009; Weston et al., 2009; Feo et al., 2010). Pyrethroids, with structures typically containing 2–3 asymmetric carbon atoms (chiral centers), are synthetic insecticides originally derived from pyrethrins that are produced by certain species of chrysanthemum (Cox, 2002; Feo et al., 2010). Pyrethroids are hydrophobic with organic carbon partition coefficients (K_{oc}) ranging from 10^5 to 10^6 L kg^{-1}, octanol–water partition coefficients (K_{ow}) ranging from 10^6 to 10^7, and typical water solubilities of a few μg L^{-1} (Laskowski, 2002). The phenylpyrazoles constitute a newly developed class of chemicals with insecticidal and herbicidal properties (Yanase

and Andoh, 1989; Klis et al., 1991). A common phenylpyrazole insecticide is fipronil with an average K_{oc} of 803 L kg^{-1} and K_{ow} of 10,232.9 (Mize et al., 2008), which can be transformed into the relatively toxic metabolites fipronil sulfide and fipronil sulfone (Brennan et al., 2009a,b). Previous studies have shown that some pyrethroids, including permethrin and bifenthrin, are possible human carcinogens (Cox, 1996, 1998). Risks to ecosystems are uncertain for the phenylpyrazoles due to their recent introduction (Mize et al., 2008). Due to their widespread usage and chemical properties, occurrence of some pyrethroids and phenylpyrazoles in different non-target environments is expected (Brennan et al., 2009b; Hladik and Kuivila, 2009; García-Rodríguez et al., 2010). Moreover, pyrethroid and phenylpyrazole pesticides have high toxicity to non-target organisms, with 10-day median lethal concentration (LC$_{50}$) values ranging from 2 to 140 ng L^{-1} in water (*Americamysis bahia* and *Ceriodaphnia dubia*) and 4–110 μg kg^{-1} in sediment (*Hyalella azteca*) for pyrethroids (Hladik and Kuivila, 2009); and LC$_{50}$ values ranging from 11.2 to 68.6 μg L^{-1} in water (*Procambarus clarkii*) (Schlenk et al., 2001) and 0.88–1.1 μg kg^{-1} in sediment (*Chironomus dilutus*) for fipronil and its metabolites (Brennan et al., 2009b). Recently, pyrethroid and phenylpyrazole pesticides in sediment samples have also been frequently reported (Moore et al.,

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2004; Weston et al., 2006; Woudneh and Oros, 2006; Brennan et al., 2009b; Hladik and Kuivila, 2009; Weston et al., 2009). Evaluation of pyrethroids and phenylpyrazoles in sediments is needed to evaluate their potential ecological risks.

Many extraction techniques for sediment/soil samples have been established and widely applied. These techniques include Soxhlet extraction (Bennett et al., 2000; Oudou et al., 2004; Woudneh and Oros, 2006; Hintzen et al., 2009), microwave-assisted extraction (MAE) (Esteve-Turrillas et al., 2004, 2006; Hernández-Soriano et al., 2007), and accelerated solvent extraction (ASE) (Mekebri et al., 2008; Brennan et al., 2009b; Weston et al., 2009; Wang et al., 2010; You et al., 2010). Soxhlet extraction has historically been the standard sediment extraction method, but requires a long extraction time (6–24 h), large volumes of organic solvents (Luque de Castro and García-Ayuso, 1998), and sufficient space for the apparatus. While MAE and ASE are advantageous for saving time and solvents (Ganzler et al., 1986; Richter et al., 1996), they require specialized and expensive equipment, thereby increasing the cost of extraction. Ultrasonic extraction (USE) has been widely employed (You and Lydy, 2004; You et al., 2004; Gonçalves and Alpendurada, 2005; Lesueur et al., 2008; Moore et al., 2009) due to its shorter extraction time, equipment simplicity, and procedural simplicity (Mecozzi et al., 2002). Following extraction, extracts usually are subjected to various clean-up procedures to remove co-extracted compounds that interfere with the analytical procedures. These interferences usually mask the target analytes with noise or high chromatographic baselines (You and Lydy, 2004). Addition of copper to extracts is a common method (Jensen et al., 1977; Japenga et al., 1987; Folch et al., 1996; Fernández-Escobar et al., 1998; You and Lydy, 2004) for removing interfering constitutes, including sulfur (You and Lydy, 2004), from extracts. Activated copper may be added as powder (You and Lydy, 2004), bars (Folch et al., 1996), wires (Pastor et al., 1997; Esteve-Turrillas et al., 2004), and granules (Rawn et al., 2001). Most published methods incubate the extracts with copper for several hours at room temperature (Folch et al., 1996; Pastor et al., 1997; Esteve-Turrillas et al., 2004). Several of the previously mentioned copper-based methods were evaluated by us for analysis of pyrethroid/phenylpyrazole pesticides in analytically problematic sediments collected from residential ponds in southern Florida as part of a monitoring project. None of those methods reduced the chromatographic noise to acceptable levels, making it necessary to evaluate alternative methods.

In addition to extraction and clean-up methods, sample storage time can significantly impact the recoveries of target pesticides. Under normal conditions, samples are typically stored at 4 °C or frozen if they cannot be extracted immediately (Brennan et al., 2009b). Knowledge of analyte disposition with age is necessary to determine the maximum storage time allowable without experiencing reductions in recoveries.

The objectives of the current study were to: 1) evaluate an alternative method for optimizing copper action, 2) determine the optimal conditions for clean-up of sediment extracts, 3) evaluate the influence of aging on sediment extractions, and 4) validate the performance of this method using field-collected samples from several different residential lakes. The ultimate goal was to establish a simple, effective, and laboratory friendly method for analyzing pyrethroid and phenylpyrazole pesticides in sediments.

2. Methods and materials

2.1. Standards, reagents, and chemicals

Eleven pyrethroids and phenylpyrazoles were chosen as target compounds for evaluation. The selected pesticides and stated manu-facturer purities included: cyfluthrin (also called baythroid; mixture of isomers I, II, III, and IV, purity 98%), deltamethrin (mixture of isomers,

purity 99%), cis-permethrin (purity 99.5%), trans-permethrin (purity 91.8%), bifenthrin (purity 99.0%), lambda-cyhalothrin (purity 99.1%), esfenvalerate (purity 99.5%), fenvalerate (purity 99.2%), fipronil (purity 99%) and two of its metabolites, fipronil sulfide (purity 95%) and fipronil sulfone (purity 98.2%). As described in You and Lydy (2007), several of the pyrethroid pesticides may isomerize during extraction and analysis. Results were reported for individual isomers of cyfluthrin. Results for cyhalothrin and deltamethrin were only reported for the primary peak. In the case of cyhalothrin, the first resolvable isomer was typically less than 2% of the primary peak area, and was too low to accurately quantify. The other isomers were likely unresolved within the primary peak. Likewise, the minor isomer for deltamethrin was always ≤2% of the primary peak, and was too low to accurately quantify. Standards were purchased from Chem Service (West Chester, PA, USA). Pesticides were individually dissolved in methyl tertiary butyl ether (MTBE) at different concentrations ranging from 250 to 2000 mg L^{-1} based on analytical instrument sensitivities. Standards containing a mixture of all of the individual compounds were made by mixing appropriate amounts of each individual pesticide. The surrogate for sediment samples was 4, 4'-dibromooctafluorobiphenyl (purity 98%), purchased from Sigma-Aldrich (St. Louis, MO, USA). Post-extraction surrogates included decachlorobiphenyl (neat chemical, purity 99%) and 1-bromo-2-nitrobenzene (neat chemical, purity 99%); and were purchased from Supelco (Bellefonte, PA, USA) and Restek (Bellefonte, PA, USA), respectively. Anhydrous sodium sulfate (analytical-reagent grade) was supplied by Fisher Scientific (Pittsburgh, PA, USA) and treated at 400 °C for 4 h before usage. Copper granules with purity 99.99% were purchased from Fisher Scientific (Pittsburgh, PA, USA). All solvents and other reagents used were of ACS (American Chemical Society) grade or higher.

2.2. Sample collection and handling

The sediment used for method development was collected from a residential pond in the Indian River Lagoon watershed, Saint Lucie County, FL, USA. Samples were collected from approximately the top 2.5–5 cm of the residential pond bottom using a stainless steel Ekman dredge. Sediment samples were placed in amber glass bottles on ice after collection and were held at 4 °C in the laboratory. Sediments were air dried, homogenized, sieved to <1 mm, and stored in amber glass bottles at 4 °C until extracted. The organic carbon (OC) in the sediments was determined using a C/N analyzer (Vario MAX CN Macro Elemental Analyzer, Elemental Elementar Analysensysteme GmbH, Hanau, Germany) and EPA Method 415.1 (USEPA, 1979). The levels of sand, silt, and clay in sediment were determined employing the hydrometer method (Day, 1965).

2.3. Ultrasonic extraction procedure

All extractions were performed using a 50–60 Hz ME 2.1 ultrasonic cleaner (Mettler Electronics Corp., Anaheim, CA, USA). Five grams of prepared sediment were weighed into a 40-mL glass vial. Next 40 µL of the 0.25 mg L^{-1} 4, 4'-dibromooctafluorobiphenyl surrogate solution was added to every sample, and 40 µL of pyrethroids/phenylpyrazoles mix (0.25–2.0 mg L^{-1}) were added to a matrix spike (MS) and matrix spike duplicate (MSD). A method blank (MB), instrument blank (IB), MS, MSD, and quality control check standard from a second source were always included in each batch of samples. Five grams of anhydrous sodium sulfate was next added to remove water from the samples, followed by the addition of 20 mL of the acetone/methylene chloride extraction solvent mixture (1:1, v/v CH_3COCH_3/CH_2Cl_2 (You et al., 2004; Wang et al., 2010)). The samples were then ultrasonically extracted at room temperature for 15 min. The sonication procedure was repeated twice and the extracts from each time were combined into a safety-coated clear wide-mouth jar (7 cm in diameter, 250 mL).