



Analysis of sediment-associated insecticides using ultrasound assisted microwave extraction and gas chromatography–mass spectrometry

Huizhen Li^{a,b}, Yanli Wei^{a,b}, Jing You^{a,*}, Michael J. Lydy^c

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

^c Fisheries and Illinois Aquaculture Center and Department of Zoology, 171 Life Science II, Southern Illinois University, Carbondale, IL 62901, USA

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ABSTRACT

An ultrasound assisted microwave extraction (UAME) method was developed to simultaneously extract five organophosphate (OP) and eight pyrethroid insecticides from sediment. The optimized UAME conditions were to use 100 ml of a mixture of hexane and acetone (1:1, v/v) solution as the extraction solvents, and extraction time, microwave and ultrasonic power settings of 6 min, 100 W and 50 W, respectively. Extracts were cleaned using solid phase extraction and analyzed by gas chromatography–mass spectrometry in negative chemical ionization mode and quantification was based on matrix-matched standard solutions along with internal standard calibration. At the spiked concentrations of 1, 5 and 20 ng/g dry weight (dw), recoveries of OPs were 77.6–122%, 65.2–128% and 75.6–141% with relative standard deviations (RSDs) of 10.6–18.1%, 3.1–12.5% and 8.0–35.3%, respectively, while recoveries of pyrethroids were 78.0–101%, 76.4–104% and 71.0–99.5% with RSDs of 10.3–23.5%, 4.7–17.6% and 8.8–18.7%, respectively. Method detection limits ranged from 0.31 to 0.45 ng/g dw for the OP insecticides and from 0.27 to 0.70 ng/g dw for the pyrethroid insecticides. The newly developed UAME method was validated by comparing it to Soxhlet and sonication extraction methods. Better recoveries were achieved for most OPs by the novel UAME method, whereas there was no significant difference in recoveries for most of the pyrethroids. Finally, the UAME method was used to quantify the target insecticides in field-contaminated sediment samples which were collected in Guangzhou, China.

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1. Introduction

Organophosphate (OP) and pyrethroid insecticides are currently used for pest control in both agricultural and urban areas in China, and their residues are transported to the aquatic environment through runoff events [1]. These insecticides strongly bind to sediment; therefore, their degradation rates are reduced, and as a result, sediment becomes a reservoir for these compounds, and analysis of sediment samples for insecticides is an effective method to quantify insecticide contamination [2].

Due to the strong binding between insecticides and sediment organic carbon (OC), it generally requires an exhaustive extraction method to separate analytes from the complicated matrix components. Different methods have been developed to extract OP and pyrethroid insecticides from sediment [3–11]. Since its introduction in 1879, Soxhlet extraction is still widely used because of its acceptable extraction efficiency and low cost [3]. However, the lengthy extraction time (from 4 to 48 h) which may lead to

potential loss of analytes as well as the requirement of large extraction solvent volumes stimulated studies examining alternative extraction techniques. Sonication extraction [4,5], supercritical fluid extraction (SFE) [6], microwave-assisted extraction (MAE) [7,8] and accelerated solvent extraction (ASE) [9–11] have been employed to extract insecticides from sediment. Although these alternative methods greatly reduced extraction time and solvent usage, most of them, including SFE, pressurized-MAE and ASE, require operation under high pressure which requires sophisticated and expensive instruments.

In contrast, sonication equipment is relatively inexpensive, and has been shown to be an effective technique to extract organic contaminants from solid samples [4,5]. In addition to sonication, MAE operated under atmospheric pressure is another relatively low cost alternative extraction method [12,13]. Since its first introduction in 1986 [14], MAE has been used for extracting organic pollutants from various environmental matrices [12,13,15]. Two types of MAE have been developed, namely focused MAE (FMAE) and pressurized MAE (PMAE), corresponding to an open-style system under atmospheric pressure and a closed-style system under a certain pressure, respectively [16]. The PMAE method has been extensively used since it can simultaneously extract multiple samples, extraction time is exten-

* Corresponding author. Tel.: +86 20 8529 1497; fax: +86 20 8529 0706.

E-mail address: youjing@gig.ac.cn (J. You).

sively reduced by conducting extraction at elevated temperatures, and because PMAE has been adopted as one of the U.S. EPA standard extraction methods [15–18]. On the other hand, the application of FMAE has been less studied [12,13,19]. By performing extractions under atmospheric pressure, FMAE may provide solutions for some of the limitations of PMAE, such as the high instrumentation cost, lengthy cooling time, low sample load, possibility of losing relatively volatile analytes and degradation of labile compounds at high temperature [16]. Additionally, temperature is controlled by the boiling point of the solvent under atmospheric pressure in FMAE, which guarantees more precisely controlled energy delivery [13].

Considering the improved heating delivered by microwave extraction and efficient agitation provided by ultrasound, the combination of the two techniques produced high yields in short reaction time during organic synthesis [20]. However, only a few studies have combined these two techniques as an extraction tool [21–25], and no studies have used sediment as the environmental matrix. Therefore, the objective of the present study was to develop and evaluate an ultrasound assisted microwave extraction (UAME) method to extract five OP and eight pyrethroid insecticides from sediment under atmospheric pressure. The UAME method was optimized using a four-factor-three-level orthogonal fractional factorial experiment and the developed method was validated by applying it to sediment spiked with the target insecticides at different concentrations. The UAME method was also compared to traditional Soxhlet and sonication extraction techniques. Finally, field sediments collected from Guangzhou, China were analyzed with the newly developed UAME method.

2. Experimental

2.1. Chemicals and materials

Five organophosphate (OP) and eight pyrethroid insecticides were analyzed in the present study. The OPs used included chlorpyrifos, diazinon, malathion, terbufos, and tebufos, while the pyrethroid insecticides included bifenthrin, *lambda*-cyhalothrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, permethrin, and tefluthrin (Table 1). These particular insecticides were selected, because they are currently used in the Pearl River Delta, China. Tefluthrin was purchased from Sigma–Aldrich (St. Louis, MO, USA) and had a purity of 96.8%, and chlorpyrifos with a purity of 97% was obtained from Ultra (Kingstown, RI, USA). The remaining insecticide standards were purchased from ChemService (West Chester, PA, USA) and had purities >97% as certified by the manufacturer.

Decachlorobiphenyl (DCBP) and 4,4'-dibromooctafluorobiphenyl (DBOBF) were used as surrogates and added to the sediment samples prior to extraction to verify the performance of the analytical process and were purchased from Supelco (Bellefonte, PA, USA). Parathion-*d*₁₀ (Cambridge, Andover, MA, USA) and PCB 189 (AccuStandard, New Haven, CT, USA) were used as internal standards (IS), and were added to the solutions before GC/MS analysis to quantify the OPs and pyrethroids, respectively. The stock solution of each insecticide and surrogate was made at 1 mg/ml in hexane.

Hexane (HPLC grade) was purchased from Burdick and Jackson (SK Chemicals, Ulsan, Korea). Analytical grade dichloromethane and acetone were purchased from Tianjin Chemical Reagent Company (Tianjin, China) and re-distilled in a glass system. Copper powder was cleaned by sonication using acetone, and anhydrous sodium sulfate was baked at 450 °C for 4 h prior to use. Dual-layer solid phase extraction (SPE) cartridges, which were packed with 600 mg primary/secondary amine (PSA) and 300 mg graphite carbon black (GCB), were purchased from Supelco.

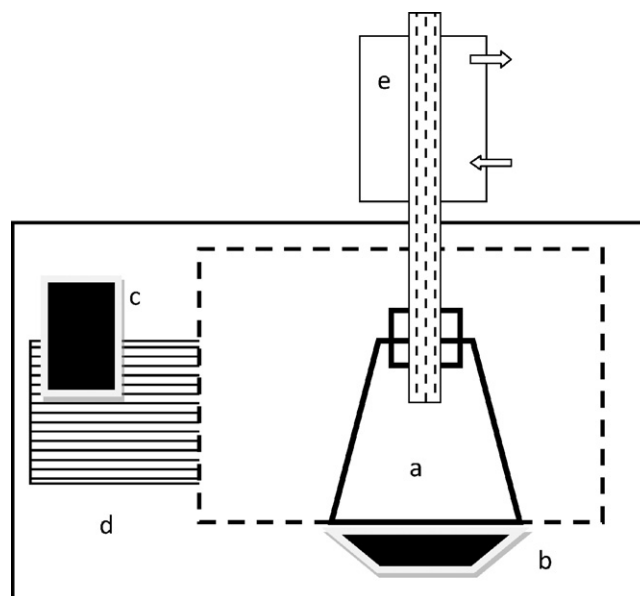


Fig. 1. Schematic diagram of the ultrasound assisted microwave extraction apparatus. (a) Sample flask; (b) ultrasound transducer; (c) microwave magnetron; (d) microwave guide; (e) condenser.

2.2. Sediment spiking and collection

The optimization of the UAME method was conducted using a reference sediment (GIG) prepared from a hydrated soil collected from the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China, whereas another reference sediment (HB) collected from Hailing Bay, China was used for method validation. No target insecticides were detected in either reference sediment. The GIG soil was air dried at room temperature, ground and sieved through a 2 mm sieve, hydrated to make sediment, and spiked with an appropriate amount of insecticide standard to obtain a concentration of 10 ng/g dry weight (dw). The spiked GIG sediment was mixed thoroughly and stored at 4 °C for 11 days before extraction. The HB sediment samples were spiked with the target insecticides at 1, 5 and 20 ng/g dw to estimate method detection limits (MDL) and assess recoveries and relative standard deviations (RSDs) at the different spiking concentrations. A separate aliquot of HB sediment was spiked at 30 ng/g dw to compare extraction efficiencies among the newly developed UAME and traditional Soxhlet and sonication extraction methods. The spiked HB sediment was thoroughly homogenized and stored at 4 °C overnight before use. All extractions were performed using four replicates; with the exception of the seven replicates used for the MDL study, where the sediment was spiked at 1 ng/g dw.

In addition, five field-contaminated samples collected from the Guangzhou Higher Education Mega Center, Guangzhou, China were used to validate the newly developed UAME method. The upper 1–2 cm of the sediment column was collected with a stainless steel scoop, sieved through a 2 mm sieve, and transported back to the laboratory. After being fully mixed, sediments were stored in the dark at 4 °C until analysis on the next day.

2.3. Sediment Extraction

2.3.1. Ultrasound assisted microwave extraction (UAME)

The UAME was performed on a CW-2000 UAME instrument (Xintuo Company, Shanghai, China) under atmospheric pressure, and the schematic diagram of this extractor is shown in Fig. 1. Ultrasound and microwave energy was provided simultaneously to the sample in the extraction flask to initiate the solvent extraction.

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