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# Stable carbon isotope fractionation during the biodegradation of lambda-cyhalothrin

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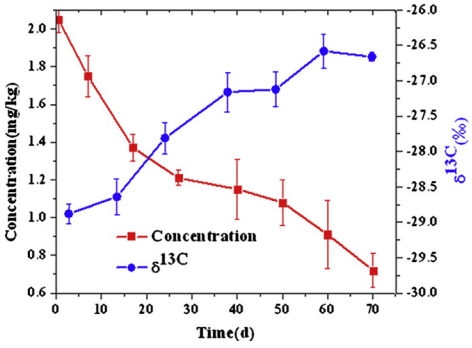
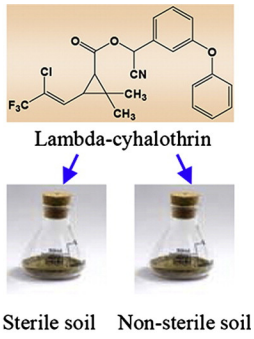
## HIGHLIGHTS

- Abiotic and biotic degradation of lambda-cyhalothrin were observed in soil.
- Biodegradation of lambda-cyhalothrin was evaluated by CSIA.
- Biodegradation of lambda-cyhalothrin leads to carbon isotope fractionation.
- An enrichment factor $\varepsilon$ of lambda-cyhalothrin was determined as −2.53‰.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this study, the microbial degradation of lambda-cyhalothrin in soil was investigated using compound-specific stable isotope analysis. The results revealed that lambda-cyhalothrin was biodegraded in soil under laboratory conditions. The half-lives of lambda-cyhalothrin were determined to be 49 and 161 days in non-sterile and sterile soils spiked with 2 mg/kg lambda-cyhalothrin and 84 and 154 days in non-sterile and sterile soils spiked with 10 mg/kg lambda-cyhalothrin, respectively. The biodegradation of lambda-cyhalothrin resulted in carbon isotope fractionation, which shifted from −29.0‰ to −26.5‰ in soil spiked with 2 mg/kg lambda-cyhalothrin, and to −27.5‰ with 10 mg/kg lambda-cyhalothrin. A relationship was established between the stable carbon isotope fraction and the residual concentrations of lambda-cyhalothrin by the Rayleigh equation in which the carbon isotope enrichment factor $\varepsilon$ of the microbial degradation of lambda-cyhalothrin in the soil was calculated as −2.53‰. This study provides an approach to quantitatively evaluate the biodegradation of lambda-cyhalothrin in soil in field studies.



## 1. Introduction

As a pyrethroid insecticide characterized by a broad spectrum of impact for insects, high efficiency, and low toxicity for mammals (Katsuda, 1999), lambda-cyhalothrin has been widely used to control insect pests, including aphids and coleopterous and lepidopterous

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pests, in cotton, cereals, hops, ornamentals, potatoes, vegetables, and flowers in agriculture, gardens and homes (Amweg and Weston, 2005; He et al., 2008). In addition, the pesticide has been applied to control cockroaches, mosquitoes, ticks, and flies in public health management (Gu et al., 2007). With a wide application in various fields, the residue of lambda-cyhalothrin has been detected in many environmental matrices. For example, its concentration in water has been reported to be 0.11–0.14 μg/L in agricultural watersheds in Stanislaus County, CA, USA, and its concentration in soil ranges from 0.003 to 0.315 μg/g dry weight (He et al., 2008). Considering the toxicity of lambda-cyhalothrin on non-target organisms, such as acute toxicity on aquatic organisms (Gu et al., 2007; Wang et al., 2007; Xu et al., 2008) and immunotoxicity and endocrine disruption on mammal cells (Zhao et al., 2008, 2010), the lambda-cyhalothrin residue in the environment is a challenging issue.

Previous studies have reported various metabolism of lambda-cyhalothrin, including photolysis, hydrolysis, and microbial degradation (Fernandez-Alvarez et al., 2007; Gupta et al., 1998; Wang et al., 1997). In soil, biodegradation primarily contributes to the dissipation of lambda-cyhalothrin, according to laboratory studies (Wang et al., 1997). However, the biodegradation of lambda-cyhalothrin in situ can be difficult to evaluate due to the interference of abiotic processes, such as photolysis and hydrolysis and dilution. Abiotic processes also lead to the attenuation of lambda-cyhalothrin in soil, even when the determination of metabolites is involved. One approach used to monitor biodegradation is compound-specific stable isotope analysis (CSIA).

Microorganisms are inclined to utilize the lighter isotopes of compounds in microbial degradation, resulting in the enrichment of heavier isotopes in the residual fraction (Gelman and Binstock, 2008). In contrast, abiotic degradation typically does not significantly change the isotope ratios of the compounds (Slater et al., 2000; Huang et al., 1999). CSIA has been used to detect and quantify the isotope enrichment of compounds undergoing biodegradation, thus assessing the extent of in situ biodegradation of the compounds (Meckenstock et al., 2004; Fletcher et al., 2009; Vieth et al., 2003). In most cases, compound-specific stable carbon isotope analysis has been employed to provide insight into the fate and transformation of compounds instead of other elements, such as hydrogen and chlorine, due to the reduced cost, higher precision, and limitation of the instrument (Morasch et al., 2001).

To the best of our knowledge, the biodegradation of lambda-cyhalothrin has not been studied by CSIA to date. In this study, we quantitatively evaluated the biodegradation of lambda-cyhalothrin by CSIA in soil. The shift in the carbon isotope ratio was observed after biodegradation and the enrichment factor $\varepsilon$ of lambda-cyhalothrin was determined for the first time. Furthermore, the potential of lambda-cyhalothrin for microbial biodegradation was also estimated in soil. This study will provide an approach to quantitatively evaluate the biodegradation of lambda-cyhalothrin in in situ contamination and repair.

## 2. Materials and methods

### 2.1. Reagents and materials

The lambda-cyhalothrin standard (≥97%) was purchased from Nanjing Rong Qin Chemical Co., Ltd. (Nanjing, Jiangsu, China). Hexane (>99.9%) and acetone (>99.4%) were of pesticide residue grade and were obtained from Mreda Technology Inc., USA and Mallinckrodt Baker Inc., USA, respectively. Anhydrous sodium sulfate was purchased from Jiangsu Qiangsheng Chemical Ltd. Florisil (0.15–0.25 mm) and silica gel (60–200 μm) was purchased from Sigma-Aldrich Inc., USA, and Acros Inc., Belgium, respectively. Lambda-cyhalothrin was dissolved in acetone at a stock concentration of 100 mg/L.

The soil samples were collected from a farmland (0–10 cm) in Quzhou City, Zhejiang Province, China. The organic matter, pH, and water content were determined to be 1.12%, 4.77, and 72%, respectively. The soils were air-dried and passed through a 2-mm sieve before use.

### 2.2. Dissipation in soil

The dried soil (5 g) was added into a 50-mL Erlenmeyer flask and adjusted to 60% moisture with ultra-pure water. The soil samples were incubated away from direct sunlight at 30 °C for 2 weeks to activate the soil microorganisms. Another group of soil samples was intermittently sterilized using three rounds of high pressure steam sterilization to completely inactivate the soil microbes. Working solutions of lambda-cyhalothrin were prepared at 10 and 50 mg/L from the stock solution. Each working solution (1 mL) was added to the flask with active or sterilized soil and then mixed. All of the soil samples were incubated under the conditions same with activation of soil microorganisms described above. In the incubation, appropriate distilled water was added to maintain initial moisture. The lambda-cyhalothrin residue in the soil was determined every 10 days. Each determination was performed in triplicate.

### 2.3. Soil sample extraction and cleanup

The soil from each flask was mixed with anhydrous sodium sulfate and Soxhlet-extracted with 160 mL of hexane/acetone (v/v, 3:1) for 24 h. The extract was then concentrated to approximately 2 mL and subjected to clean up. The extract was loaded onto a glass column packed with 2 g of anhydrous sodium sulfate, 5 g of florisil, 3.5 g of silica gel, and 2 g of anhydrous sodium sulfate from bottom to top. The column was eluted with 60 mL of hexane/acetone (v/v, 9:1). The elute was concentrated to nearly dryness and re-dissolved in 1 mL of hexane for the GC-MS analysis. After the GC-MS analysis, the extract was concentrated to nearly dryness again and re-dissolved in 50 μL of nonane for the GC-C-IRMS analysis.

### 2.4. Analysis of lambda-cyhalothrin by GC-MS

The lambda-cyhalothrin residue was determined using a GC-MS (Agilent 7890A-5975C) equipped with an HP-5 ms column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent J&W GC columns). Helium (purity ≥ 99.999%) was used as the carrier gas at a flow rate of 1 mL/min. One microliter of extract was injected in splitless mode. The injection temperature was 260 °C. The oven temperature was initially 100 °C, ramped to 260 °C at a rate of 20 °C/min, held at 260 °C for 8 min, climbed to 280 °C at 20 °C/min, and held there for 12 min. The MS was operated in selected ion monitoring (SIM) mode, and characteristic fragment ions (m/z = 181, 197, 208) were used for the lambda-cyhalothrin analysis. The recovery of lambda-cyhalothrin was checked by spiking of 2.5 or 25 ppm concentration in blank soil and determined as 90.71–118.5%. The relative standard deviation was 7.26%–9.78%.

### 2.5. Compound-specific stable carbon isotope analysis

Stable carbon isotope analysis of lambda-cyhalothrin in the extract was performed using an Agilent 7890A GC coupled to a GV Isoprime IRMS (GV Instruments, UK) via a modified GC5 combustion interface. An aliquot of 2.0 μL of extract was injected in splitless mode. Separation of the target compound was also achieved on an HP-5 ms column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent J&W GC columns). The oven temperature program was identical to that of the GC-MS analysis of lambda-cyhalothrin. The combustion furnace was equipped with CuO wires to oxidize the separated hydrocarbons to $CO_2$ and $H_2O$ at 850 °C. After the co-generated water vapor was removed via a Na fion trap, the $CO_2$ was swept via an open split assembly into the isotope ratio mass spectrometer in which the carbon isotope composition was measured. All isotope data were reported using the conventional delta notation ($\delta^{13}C$), giving the per mil (x) deviation of the isotope ratio of the sample relative to the Vienna Pee Dee Belemnite (VPDB) standard.