



# Dissipation and metabolism of tebufenozide in cabbage and soil under open field conditions in South China



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## ABSTRACT

The novel nonsteroidal ecdysone agonist tebufenozide is capable of controlling a wide range of lepidopteran pests. However its intensive use in vegetables has raised concerns towards the safety of food and environment. Here, we developed an easy and reliable method to analyze tebufenozide in cabbage and soil by reversed-phase high performance liquid chromatography (HPLC). The average recoveries of tebufenozide ranged from 72.01% to 101.10% with the relative standard deviations (RSD) < 6%, and the LOD and LOQ were 0.02  $\mu\text{g g}^{-1}$  and 0.05  $\mu\text{g g}^{-1}$ , respectively. According to the dissipation study, the half-lives of tebufenozide were 2.96 and 4.08 d in cabbage and 4.95–7.70 d in soil, respectively. The final residues were determined below the maximum residue limit (MRL) (0.5  $\text{mg kg}^{-1}$ ) after a pre-harvest interval (PHI) of 7 d. Moreover, its major metabolites were identified by liquid chromatography tandem mass spectrometry (LC–MS/MS) on LTQ–Orbitrap XL, which leading to the first report of the degradation pathway of tebufenozide in cabbage. The present study is expected to provide basic data for the use guidance and safety evaluation of tebufenozide in agricultural crops and environment.

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## 1. Introduction

Newly-developed nonsteroidal ecdysone agonist tebufenozide (also known as RH-5992) that imitates the action of natural molting hormone, 20-hydroxyecdysone (20E) exhibits promising efficacy in the control of lepidopteran pests which feed on a wide range of vegetables and crops (Jia et al., 2009; Retnakaran et al., 2001; Smagghe and Degheele, 1994; Sridhara and Lee, 2013). Generally, tebufenozide was regarded as a safe substance for the environment under normal operational conditions (Abass; Addison, 1996; Dhadialla et al., 1998; Dhadialla and Jansson, 1999). For instance, most toxicity tests on non-target aquatic organisms were executed with tebufenozide formulations, which indicating high substance concentrations were required to make a toxicological effect (Pauli et al., 1999; Song et al., 1997). However, intensive use has recently raised increasing resistance of tebufenozide in several pest species including *Plutella xylostella* (Cao and Han, 2015; Jia et al., 2009), *Diatraea saccharalis* (Akbar et al., 2008) and *Cydia pomonella* (Ioriatti et al., 2007). To deal with the potential resistance, tebufenozide has been mixed with other compounds, such as tebufenozide with phoxim (He et al., 2016) and

flubendiamide (Jili et al., 2014). But, compared to the wide use of tebufenozide, the newly-developed mixed formulations with limited options seem to be insufficient to eliminate all the concerns. On the other hand, the pesticide residues in field crops have become the main contributor to human exposure and their impacts in terms of human toxicity are largely underestimated (Fantke et al., 2012; Fantke and Jolliet, 2016). Besides the acute poisonings, such as seizures, rashes, and gastrointestinal illness, various chronic effects have been thought to be associated with the exposure to pesticides. Extensive researches indicated that the active ingredient of pesticides or the other ingredients in the formulations could induce dermatologic, neurologic, reproductive and genotoxic impacts to human health (Alavanja et al., 2004; Kumar et al., 2014; Meza-Montenegro et al., 2013; Sanborn et al., 2007). Therefore, the environmental monitoring of tebufenozide and its intermediate products in raw agricultural crops should be measured to ensure environmental and public health safety (Karmakar and Kulshrestha, 2009; MacLachlan and Hamilton, 2010).

Studies on the dissipation processes of pesticides and related metabolism provide a clear understanding on their environmental behaviors, which is an important issue in environmental monitoring as well as food safety assessment. Specifically, the term dissipation is defined as a composite of processes describing volatilization, wash-off, leaching, hydrolysis, chemical and biological degradation, and other individual processes reducing the amount of a pesticide in plants after application (Fantke and Juraske, 2013).

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In general, according to the residual amount on substances (such as plant, soil or water), the overall dissipation of pesticides is measured to determine the half-lives of pesticides, which are usually related to the tested substances or plant species (Fantke et al., 2014; Fantke and Juraske, 2013; Jacobsen et al., 2015). The analyzing methods employed for pesticide residues have been widely reported, most of which were based on chromatographic strategies such as high performance liquid chromatography (HPLC) (Liu et al., 2010; Malhat et al., 2014; Satheshkumar et al., 2014), liquid chromatography mass spectrometry (LC–MS) (Chen et al., 2014; Dong et al., 2015; Mandal et al., 2014; Qin et al., 2015; You et al., 2014), gas chromatography–mass spectrometry (GC–MS) (Bresin et al., 2015), gas chromatography–vacuum ultraviolet spectrometry (GC–VUV) (Fan et al., 2015) and ultra high performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UHPLC–QqQ–MS/MS) (Martínez-Domínguez et al., 2015). In recent decades, HPLC has been generally used as an excellent analyzing technique, especially for its ability to separate and quantitate residues of polar, nonvolatile, and heat-labile chemicals. In terms of tebufenozide, HPLC was commonly employed to determine its residues in food, plants and environment (Likas and Tsiropoulos, 2011; Liu et al., 2011; Smirle et al., 2004). Due to its precision, versatility, relatively low cost and suitable technique for the determination of polar analytes (Guo et al., 2010), reversed-phase HPLC was employed to determine the residues of tebufenozide in cabbage and soil. On the other hand, the accumulation of pesticides and their intermediates become more and more concerned. In order to obtain more data about their environmental behavior, there is a growing interest about the metabolism of pesticides in agricultural products under field condition. For its high mass resolution and reliable mass accuracy, liquid chromatography coupled with electrospray ionization hybrid linear trap quadrupole orbitrap (LC–LTQ–Orbitrap) mass spectrometry has proven to be a powerful and reliable analytical tool for the identification of *in vivo*- and *in vitro*-generated drug metabolites (Cai et al., 2015; Herebian et al., 2010).

Chinese cabbage is a major vegetable in northeastern Asia, such as Korea, China, and Japan. Specially, it has been an important leafy vegetable widely grown in South China in summer and autumn (Min-sheng and Guang, 2001). In this study, first we aimed to develop a valid method to analyze tebufenozide in cabbage and soil based on two techniques (HPLC and LC–LTQ–Orbitrap). Second, the dissipation process and terminal residues of tebufenozide in cabbage and soil located in southern China were investigated comprehensively. Third, some reports have described the metabolites of tebufenozide in environmental samples such as soil and water (Sundaram and Nott, 1995). To our knowledge, this is the first time to study its metabolic pathway in cabbage under open field condition (Fantke and Juraske, 2013), which would be helpful to enhance the proper and safe use of this insecticide.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Tebufenozide (CAS No. 112410-23-8) standard with 99.7% purity purchased from Yangzhou Pesticide Factory, China. The commercial formulation of 20% SC (suspension concentrate) tebufenozide was purchased from Shandong Weifang binary Pesticide Company, China. All the organic solvents were HPLC grade from ANPEL scientific instrument Shanghai, China.

Florisil (pesticide grade, 60–100 mesh) was purchased from CNW technologies GmbH (Dusseldorf, Germany); neutral alumina was obtained from Supelco (Bellefonte, USA); silica gel (60–100 mesh) was obtained from Silicycle (Quebec, Canada). Anhydrous

sodium sulfate was heated at 150 °C for six hours. The suitability of the solvents was ensured by running reagent blanks before analysis.

### 2.2. Preparation of standard solutions

Standard stock solution of 100 µg mL<sup>-1</sup> tebufenozide was prepared in methanol. The working standard solution was prepared by dilution the stock solution of the tebufenozide at different concentrations (0.5, 1 and 2 µg mL<sup>-1</sup>) to determine the retention time. A series of standard solutions were prepared at different concentrations, ranged between 0.02 and 2 µg mL<sup>-1</sup>, to study the linear regressions, limit of detection (LOD), limit of quantification (LOQ), and the recovery of the tebufenozide. All standard solutions were stored at 4 °C prior to use.

### 2.3. Method validation

The experimental method was validated by determining linearity, specificity, accuracy, precision, limit of detection (LOD) and quantification (LOQ), respectively. Linearity was accessed by constructing calibration curves using different concentrations of standard solutions (0.02–2 µg mL<sup>-1</sup>). The LOD (µg g<sup>-1</sup>) of tebufenozide was determined as the lowest concentration giving a response three times the standard deviation of the baseline noise defined based on the analysis of three control samples. The LOQ (µg g<sup>-1</sup>) was determined as the lowest concentration of a given compound giving a response that could be quantified with RSD lower than 20%. The recovery of tebufenozide was investigated to examine the reliability and validity of analytical method adopted. The recovery of tebufenozide was carried out by spiking samples of Chinese cabbage and soil without pesticide residues fortified with an analytical solution containing the insecticides at four different concentration levels (0.05, 0.1, 0.5 and 1 µg g<sup>-1</sup>) with six replicates for each level. The precision of recovery assays was estimated from relative standard deviation and the accuracy from the standard deviation for each sample.

### 2.4. Field experiment design

The dissipation behavior, final residue patterns and metabolites of tebufenozide were carried out on the farm of South China Agriculture University, Guangzhou, South China, which were previously investigated to be free of pesticide. The physicochemical properties of the soils were (g kg<sup>-1</sup> of dry weight): organic matter, 10.5; total N, 0.5; total P, 0.4; total K, 18.2; and pH, 6.9. The soils have a sandy loam texture (sand, 65.0%; silt, 28.0%; clay, 7.0%) (Chen et al., 2012). The average temperature during field experiments was 28 °C. The test fields were separated by 1 m buffer zone to avoid cross contamination. Each field was further divided into two major positions separated by 1 m buffer zone. Each position have one control plot for blank analysis and recovery experiments and three sub plots having area 2 × 1.5 m. Each of these subplots had five rows of plants, plant to plant spacing (P × P) 25 cm and row to row (R × R) distance 30 cm, with total of about 40 plants in one sub plot. Field management was carried out according to local methods to ensure the reliability of the experimental results.

### 2.5. The dissipation of tebufenozide

Cabbage for experimental use was planted in September 2015. To study the residues dynamic of tebufenozide, the cabbage at precupping stage (approximately 13–18 leaves) was sprayed with tebufenozide formulation (20% SC) at single application at 70 and 140 g hm<sup>-1</sup> (twice as the recommended dosage), respectively. Samples (cabbage and soil) were collected from the four replicates

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