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The dissipation of ethofenprox in cabbage and soil under open conditions

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Abstract The dissipation of ethofenprox in cabbage and soil under open conditions was investigated at two primary cabbage-growing regions, Beijing and Kunming in China. Samples were extracted with acetonitrile and determined by ultra-performance liquid chromatography with a single quadrupole detector. Dissipation of ethofenprox from cabbage and soil can be best explained by a first-order decay process. The half-lives of ethofenprox were 1.9 and 2.3 days in cabbage and 20.0 and 13.0 days in soil at Beijing and Kunming, respectively. The concentration of ethofenprox residue was reduced by 90% taking 7 and 60 days in cabbage and soil. Dissipation rates in cabbage and soil at two geographically separated experimental fields differed, suggesting that this was affected by complicated factors, such as local climate and soil characteristics. These data could provide guidance for the proper and safe use of this pesticide on cabbage in China.

Keywords Ethofenprox · Cabbage · Soil · Dissipation

Introduction

Ethofenprox, 2-(4-enthoxyphenyl)-2-methylpropyl-3-phenoxybenzl ether (Fig. 1), which belongs to the pyrethrin group, is widely used because of its properties of broad-spectrum insecticide control, high insecticidal activity, and safety to plants. It is usually employed to prevent and control insects with sucking mouth parts, particularly planthopper, leafhopper, aphid, and thrips on crops such as rice, fruit trees, cotton, and vegetables (Cao et al. 2010). As a systemic insecticide, it can be absorbed by roots and leaves and transmitted to the plant tissues. Therefore, ethofenprox might cause food contamination and is a potential threat to human health (Qian et al. 2011).

Cabbage is a principal leafy vegetable in many countries which is consumed every day and is simply washed before cooking or being eaten directly. However, it is often damaged by many kinds of insects and pathogens, including *Plutella xylostella, Pieris rapae*, and *Spodoptera exigua* (Wang et al. 2005). Since agricultural use of ethofenprox to control these insects has increased, appropriate maximum

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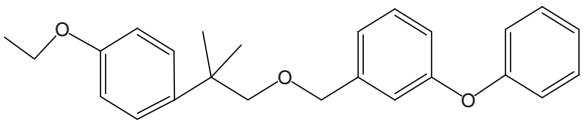

Fig. 1 Molecular structure of ethofenprox

residue limit and pre-harvest interval measurements are required to ensure food and environmental safety at harvest time. Consequently, field dissipation studies on the persistence of the pesticide in cabbage and soil are needed.

To our knowledge, limited studies have been published on the determination or dissipation of ethofenpfox. Wang studied the composition route and efficacy of ethofenprox against insects (Wang et al. 2005). Zhang introduced a quantitative analysis method of ethofenprox using gas chromatography (GC) with a glass chromatographic column (Zhang et al. 2001). Gong reported its residue in environmental and biological samples using GC, in which samples were extracted with acetone and acetonitrile saturated with petroleum ether (Gong et al. 1996). Ji developed an ultra-performance liquid chromatography with mass spectrometry method for the determination of ethofenprox residue in cabbage and soil (Ji et al. 2010). However, the dissipation of ethofenprox in agricultural fields and the influencing factors have not been discussed which are essential for evaluating its persistence and fate in the environment.

The purpose of this research was (1) to evaluate the dissipation rate of ethofenprox under field conditions and (2) to discuss factors that influence the decline of ethofenprox in cabbage and soil at two locations.

Materials and methods

Chemicals and solvents

Ethofenprox standard (purity at 98.0%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All of the reagents, including acetonitrile, sodium chloride, and other solvents were of analytical grade.

The physical and chemical properties of ethofenprox are as follows: vapor pressure of 32 mPa (100°C); solubility in water of <1 mg/kg (25°C); $\log P_{ow}$ of 7.05 (25°C). It is stable in acidic and alkaline conditions.

Field locations

Field experiments were conducted at two cabbage-growing farms in different regions of China: Tongzhou, Beijing (116.25° E, 39.92° N) and Kunming, Yunnan (102.42° E, 25.04° N). None of the farms had been treated with ethofenprox or structurally similar compounds in the past. The field studies were conducted in 2010.

Experimental design for ethofenprox dissipation evaluation

To evaluate the dissipation of ethofenprox in cabbage and soil, field experiments were carried out at two cabbage plots (one as a control) and two soil plots (one as a control) with areas of 45 m^2 each. Each plot was divided equally into three trials as three replications. In these two places, the cabbage plants were spaced 35 cm apart in a row and with 30 cm between the rows. During the experimental periods, routine weather practices were recorded. To study the ethofenprox dissipation on cabbage, the ethofenprox 10% emulsion in water formulation was sprayed on each trial at a dose of 120 g a.i./ha on 23 April 2010 in Beijing and 27 August 2010 in Kunming. The untreated cabbage plot and soil plot were sprayed with the same amount of water as the control group.

Cabbage samples were collected at 0 (3 h after application), 1, 2, 3, 5, 7, 10, 14, 21, and 28 days after application (DAA). They were harvested randomly from each replicate, and the overall sample weight was 1–2 kg. Soil samples were collected randomly from the surface soil (0–10 cm) on the days 0, 1, 3, 7, 10, 14, 21, 30, 45, 60, and 90 using a coring device (5 cm in diameter). At least 1 kg of soil from each trail was collected. Stones and plant debris were manually removed. Cabbage and soil samples were taken to the laboratory and subdivided into 50 g aliquots as analytical replicates. All of the samples were stored in individual bags at −20°C until extraction.

Sample preparation

The prepared cabbage or soil samples (20 g) were weighed into a 250-mL conical flask with a stopper. Samples were extracted with acetonitrile (40 mL) and shaken for 30 min on an oscillator. The extracts were

filtered with medium-speed qualitative filter paper into a 50-mL mixing cylinder with a stopper. Five grams of sodium chloride was added, and the mixture was shaken for 2 min and allowed to place for 10 min. After layering, 2-mL aliquot of the upper extract was transferred into a 25-mL flat-bottomed flask and concentrated to near dryness on a rotary vacuum evaporator at 40°C for further purification.

Acetonitrile (5 mL) and ultrapure water (10 mL) were used to condition an SPE-C_{18} column (3 mL, 500 g, J.T.BAKER). The concentrated extracts were transferred completely to the column with 9 mL acetonitrile/water (80/20, *v*/*v*). The first 4 mL of the elution was discarded. The remaining 5 mL was collected and filtered through a 0.22-μm membrane filter which was analyzed immediately by ultra-performance liquid chromatography coupled with a single quadrupole detector.

Instrumental analysis

An ultra-performance liquid chromatography (Waters Co.) equipped with an SQD was used for ethofenprox analysis. An ACQUITYU PLCBEH C_{18} column (2.1 mm×50 mm×1.7 μm) was used to separate the compounds, and the column temperature was maintained at 40°C. The mobile phase was composed of acetonitrile/water (80/20, *v*/*v*) with 0.1% formic acid. The flow rate was 0.4 mL/min with an injection of 5 μL. Ethofenprox was eluted at a retention time of 1.4 min.

Mass spectrometery conditions

Electrospray ionization with positive ion collection was performed with a capillary voltage of 3.0 kV and a taper hole voltage of 25 V. The temperatures of the ion source and desolvatization were 140 and 400°C, respectively. The gas flow rates of the desolvatization and the taper hole were 800 and 30 L/h under selective ion monitoring mode at 394.34 (Ji et al. 2010).

Results and discussion

Ethofenprox dissipation in cabbage and soil from two different locations are shown in Figs. 2 and 3. As expected, a gradual and continuous decline of ethofenprox residue in cabbage and soil was observed as a function of time after application. The rate equation was calculated from the first-order rate equation: $C = C_0 e^{-kt}$ where C represents the concentration of the pesticide residue at time (t), while C_0 represents the initial concentration and k is the rate constant in days. The half-lives ($t_{1/2}$) were determined from the k value for each experiment, being $t_{1/2} = \ln 2/k$. (Wang et al. 2007) The regression equation, correlation coefficient and half-lives ($t_{1/2}$) of cabbage and soil are shown in Table 1.

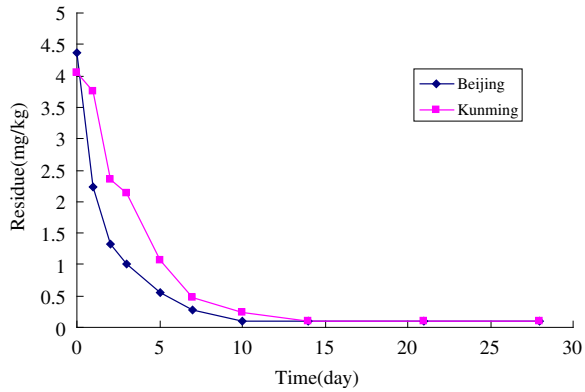

Fig. 2 Dissipation of ethofenprox in cabbage at Beijing and Kunming during 2010

Ethofenprox dissipation in cabbage

Figure 2 showed the declining trend of ethofenprox in cabbage at Beijing and Kunming during 2010. The initial concentration of ethofenprox in cabbage

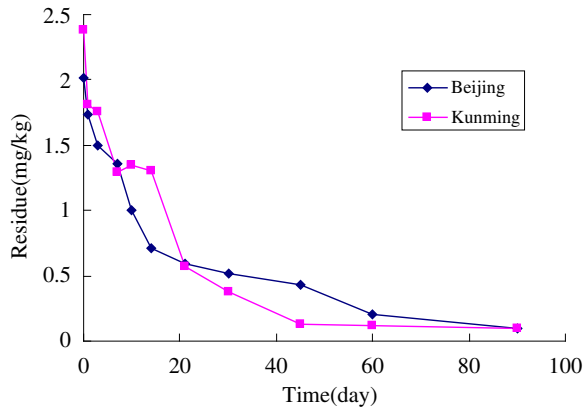

Fig. 3 Dissipation of ethofenprox in soil at Beijing and Kunming during 2010

Table 1 The regression equation, correlation coefficient, and the half-lives ($t_{1/2}$) of ethofenprox in cabbage and soil during 2010

Sample location	Sample	Regression equation	Correlation coefficient (r)	Half-life (days)
Beijing	Cabbage	$C=3.4176e^{-0.372t}$	0.9866	1.9
	Soil	$C=1.6125e^{-0.0346t}$	0.9651	20.0
Kunming	Cabbage	$C=4.5924e^{-0.3035t}$	0.9943	2.3
	Soil	$C=2.0783e^{-0.0534t}$	0.9816	13.0

differed at the two locations (4.37 mg/kg in Beijing and 4.05 mg/kg in Kunming). The largest amount of dissipation took place within 4 days after the application. One week after application, the concentration of ethofenprox residue was reduced by 93.6% in Beijing and 88.0% in Kunming. Ethofenprox residue was undetectable in cabbage after 10 days in Beijing and after 14 days in Kunming. The half-lives of ethofenprox in cabbage were 1.9 and 2.3 days in Beijing and Kunming, respectively. Because of the lack of publicly available data on the initial concentrations and half-lives of ethofenprox in cabbage, it was useful to present the data here. Indeed, our results indicate a rapid degradation and short half-life of ethofenprox in cabbage.

At these two locations, a higher initial concentration of ethofenprox was observed at Beijing than Kunming. However, ethofenprox at Beijing exhibited a shorter half-life. Since the intervals from cabbage planting to ethofenprox application were similar between Beijing and Kunming, the differences may be due to the different growth rates and environmental conditions. However, the cabbage growth had a limited effect on the ethofenprox dissipation rate, as a significant part of the dissipation occurred mostly within the 4 days after application. The cabbage was planted in April in Beijing and in August in Kunming. The differences of illumination time, illumination intensity, and rainfalls might have contributed to the different dissipation rates at the two locations.

Compared to Ji's studies in which the initial concentration of ethofenprox in Beijing was 2.74 mg/kg during 2009 (Ji et al. 2010). We got the initial concentration 4.37 mg/kg during 2010 in Beijing. However, these 2 years exhibited the same half-life (1.9 days). The similar phenomenon was also observed at Kunming, indicating that there was no relationship between the initial concentrations and half-lives. Despite the high initial concentrations, ethofenprox also decreased rapidly in cabbage.

Nakamura reported that ethofenprox is characterized by high stability against light, acids, and bases and has an extremely high bioconcentration factor of 1.6×10^6, which is higher than that of DDT by a factor of about 10 (Nakamura et al. 2002). Because of the high bioconcentration, ethofenprox may remain in living bodies or plants for a long time. However, in our study, the half-life of ethofenprox in cabbage was notably short, indicating that the bioconcentration did not play a significant role on the dissipation of ethofenprox in cabbage.

Photolysis of pesticides on plant surfaces is considered to be important to their dissipation and can be affected by various factors, including naturally occurring photosensitizers in the environment. Some photosensitizers can accelerate photodecomposition of ethofenprox (Thomas et al. 1989; Rong and Morifusa 1990) and may be an important factor leading to the rapid dissipation and short half-life of ethofenprox in cabbage.

Ethofenprox dissipation in soil

The maximum concentrations of ethofenprox in soil at 2010, measured 3 h after the application, were 2.02 mg/kg in Beijing and 2.38 mg/kg in Kunming. The residue in soil declined slower than in cabbage with the half-life of 20 days in Beijing and 13 days in Kunming. Figure 3 showed the first-order kinetics of ethofenprox in soil with a dissipation rate of 0.0346 mg/kg in Beijing and 0.0534 mg/kg in Kunming each day. At 60 DAA, the concentration was reduced by approximately 90% in the soil at two locations. Ethofenprox residue was undetectable in soil at 90 DAA in Beijing and Kunming. In this study, different soil types, pH values, and organic matter contents in Beijing and Kunming may cause different half-lives of ethofenprox in soil. These between-site differences suggest that local soil characteristics and

climate might significantly affect the dissipation of ethofenprox.

In Beijing, the initial concentrations of ethofenprox in soil were 2.02 mg/kg in 2010 with half-life 20 days and 1.49 mg/kg with half-life 37 days in 2009 (Ji et al. 2010). Photolysis of ethofenprox was reported by Rong (Rong and Morifusa 1990). The experiments were conducted from August to October in 2009 while from April and July in 2010. Different levels of sunlight might have caused varying degree of photolysis and, thus, different half-lives. The same conditions were also achieved in Kunming with an initial concentration of 1.36 mg/kg in 2009 (Ji et al. 2010) and of 2.38 mg/kg in 2010 with half-lives 17 and 13 days, respectively.

The behavior of the pesticides in soil was governed by a variety of complex dynamic physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, runoff, leaching and so on under field conditions (Fang and Qiu 2002; Zhang and Cooper 1996). These processes may directly affect the transportation of ethofenprox in soil. The relative importance of these processes varied with the chemical structures of the pesticides and properties of soil.

Gong studied the residue of three different formulations of ethofenprox on rice soil. The half-lives of three formulations (suspension concentrate, water power, and oil solution) were 9, 9, and 12 days, respectively (Gong et al. 2002). The half-lives were shorter than those in our study, which probably due to different soil characteristics, climate and formulations.

Conclusions

Based on the established method on the determination of ethofenprox, the dissipation rates of ethofenprox in cabbage and soil were studied to evaluate the proper use of this pesticide. The decline of ethofenprox from cabbage and soil fit a first-order decay process. Its residue in cabbage dissipated faster than in soil with half-lives ranging from 1.9 to 2.3 days in cabbage and 13.0 to 20.0 days in soil. The decline was influenced by various factors, and these results would be useful for related studies on ethofenprox.

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