Ecotoxicology and Environmental Safety 104 (2014) 23–27

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

# Effect of two formulations on the decline curves and residue levels of rotenone in cabbage and soil under field conditions

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ARTICLE INFO

*Article history:*
Received 28 July 2013
Received in revised form
9 February 2014
Accepted 12 February 2014
Available online 12 March 2014

*Keywords:*
Rotenone
Biopesticide
Formulation
Dissipation
Residue

ABSTRACT

The dissipation and residue levels of rotenone with suspension concentrate (SC) as well as water dispersible granule (WDG) formulations in cabbage and soil were investigated under field conditions. The decline curves of rotenone residues in cabbage and soil corresponded with first-order kinetics. The dissipation rate of rotenone in cabbage was faster than that in soil. The half-lives of the SC formulations in cabbage and soil were 1.14 d to 1.85 d and 2.26 d to 3.98 d, respectively. For the WDG formulation, the values were 1.33 d to 1.96 d and 2.41 d to 3.38 d. Less spraying, lower dosage, and longer pre-harvest intervals could reduce terminal residue levels. Terminal residues below the MRL (0.5 mg $kg^{-1}$) were achieved after pre-harvest intervals of 3 d at either once (45 g a.i. $ha^{-1}$) or twice (90 g a.i. $ha^{-1}$) the recommended dosage. The different dissipation processes of rotenone in cabbage and soil under field conditions could be attributed to the different climate and soil properties, and the types of formulation had no apparent effect on half-life. Formulation type affected the initial concentrations and finally led to different terminal residues. Prolonged pre-harvest intervals are necessary to ensure that the products are sufficiently safe for consumption.



## 1. Introduction

Rotenone, as a selective and non-specific botanical insecticide, is used for organic agriculture in Europe (Cavoski et al., 2011). Rotenone disrupts energy metabolism in cell mitochondria, either by inhibiting the electron transport system or by uncoupling the transport system from ATP production (Rameshwar, 2010). Rotenone gets converted to metabolites that are highly toxic to insects but it detoxifies in mammals (Ware, 1988). However, an increasing number of studies show that rotenone exposure has a positive relationship with Parkinson's disease and other neurological diseases in animals (Betarbet et al., 2000; Heikkila and Sonsalla, 1987; Jenner, 2001; Tanner et al., 2011).

Rotenone is a general-use pesticide. It is commercially available in the United States and Europe as wettable powders containing five percent or twenty percent of active substance, as 0.75 percent to five percent dusts, and as a five percent emulsifiable concentrate (Wiwattanapatapee et al., 2009). This pesticide is highly toxic or slightly toxic depending on formulation. It is highly toxic when formulated as an emulsified concentrate; other forms are slightly toxic (Hien et al., 2003). As early as the 1990s, suspension concentrates (SC) and water-dispersible granules (WDG) have been receiving considerable attention (Seaman, 1990). Formulations that are water-based, in particle form, multifunction, labor-saving, safe, and have a reduced environmental impact, such as SC and WDG formulations, have become a trend in pesticide development worldwide and been regarded as a new technology (Hua, 2008; Knowles, 2009). In recent years, the SC and WDG formulations of rotenone have appeared in Chinese agro-market.

There are many research articles and reviews about rotenone's chemistry, biological activity and mechanism of action and the toxicity and so on (Cavoski et al., 2011; Rameshwar, 2010; Betarbet et al., 2000; Haley, 1978; Heikkila and Sonsalla, 1987; Jenner, 2001; Tanner et al., 2011). However, studies on its environmental fate either the formulations are too old to keep up with the development of times (Newsome and Shields, 1980), or little focusing on the influence of different formulations to its dissipation and residue in the field (Zhou et al., 2013). Furthermore, different pesticide formulations always lead same active ingredient to have different half-lives and terminal residues in plant and soil (Gong et al., 2002; Liu et al., 2007; Wang et al., 2009). To evaluate the effect of formulation on rotenone residue in cabbage and soil

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http://dx.doi.org/10.1016/j.ecoenv.2014.02.014
0147-6513 

under field condition, this study would compare the rotenone dissipation rate and terminal residues of the SC and WDG formulations. This data would be helpful for the establishment of MRLs for rotenone SC and WDG products. So would the proper and safe use of them.

## 2. Materials and methods

### 2.1. Apparatus and chemicals

HPLC LC-20A equipped with an UVD and an autosampler, interfaced to LCsolution data processing software (Shimadzu, Japan). Zorbax TC-C18 column (250 mm × 4.6 mm ID), film thickness 5 μm (Agilent, American).

2.5 percent rotenone suspension concentrates (SC) and 3 percent rotenone water-dispersible granules (WDG) (Guangdong Yuentin Biological Engineering Co., Ltd., China). Acetonitrile, HPLC-grade (Oceanpak, Sweden). Rotenone certified reference standard, 97.0 percent pure (Sigma, American).

### 2.2. Field experiment

Field trials were conducted in Guangzhou (GZ), Qianjiang (QJ), and Nanning (NN), China in winter of 2011 in accordance with the "Guidelines on Pesticide Residue Trials" (NY/T 788-2004) issued by the Ministry of Agriculture, People's Republic of China.

During the experimental period, the average temperatures in Qingyuan, Qianjiang, and Nanning were 18.3, 16.5, and 13.7 °C. The corresponding rainfall events were 4, 9, and 16. Soil of Qingyuan is sandy clay loam with 17.1 g $kg^{-1}$ organic matter and pH of 6.8. Soil of Qianjiang is clay loam with 19.3 g $kg^{-1}$ organic matter and pH of 6.5. Soil of Nanning is loam with 14.2 g $kg^{-1}$ organic matter and pH of 7.1. Each experimental treatment consisted of three replicates and a control plot. A buffer (1 m distance) was set to separate each plot (15 $m^2$).

To study the dissipation of the two rotenone formulations in cabbage and soil, 2.5 percent rotenone SC and 3 percent rotenone WDG were applied at 90 g a.i. $ha^{-1}$ (twice the recommended dosage).

To investigate the terminal residue of the two rotenone formulations in cabbage and soil, 2.5 percent rotenone SC and 3 percent rotenone WDG were applied at 45 g a.i. $ha^{-1}$ (the recommended dosage) and 90 g a.i. $ha^{-1}$ (twice the recommended dosage). Each application dosage was sprayed three to four times at 7 d intervals.

### 2.3. Sample collection and storage

According to the mentioned guidelines, samples (cabbage: at least 1 kg, soil: at least six points) were randomly collected from each plot at different time intervals. Soil samples were collected using a soil auger. For the dissipation experiments, samples were collected 0, 1, 2, 3, 5, 7, 10, and 14 d after spraying, and the sampling soil depth was 10 cm. For the terminal residue experiments, samples were collected 1, 3, and 6 d after spraying, and the sampling soil depth was 15 cm. All the samples were stored at −20 °C until further analysis.

### 2.4. Analysis of rotenone residue

Cabbage samples were crushed thoroughly in a blender and soil samples were homogenized and prepared by passing through a 1 mm sieve before analysis. The rotenone residue in cabbage and soil was extracted with acetonitrile, then purified with column chromatography, and finally, analyzed using a reverse-phase HPLC. According to the analyzing method, the mean recoveries and relative standard deviations at 0.02, 0.1 and 0.5 mg $kg^{-1}$ from five replicates of blank cabbage and soil samples ranged from 81.17 percent to 93.83 percent and 3.44 percent to 9.14 percent, respectively. The LOQ was 20.3 μg $kg^{-1}$ ($S/N=10$) and LOD was 6.1 μg $kg^{-1}$ ($S/N=3$) (Zhou et al., 2013).

### 2.5. Statistical analysis

All the experiments were repeated three times. Values of half-life and terminal residue are expressed as means and means ± SD. The concentration and half-life of the rotenone residue were calculated using first-order kinetics equations $C_t=C_0e^{-kt}$ and $t_{1/2}=\ln 2/k$, respectively. Analysis of variance (ANOVA) for the effect of formulation on the dissipation rate (half-life) and terminal residues in cabbage and soil was conducted by SPSS 17.0.

## 3. Results and discussion

### 3.1. Effect of formulations on the dissipation rate of rotenone in cabbage and soil

The behaviors of the SC and WDG formulations in cabbage and soil could evidently be fitted well with first-order kinetics. Rotenone was not persistent in the environment. Almost 90 percent of rotenone SC in cabbage degraded within the first 3 d after application, and 80 percent of rotenone WDG also degraded within the same period (Fig. 1). Meanwhile 80 percent of both formulations of rotenone deposited in soil degraded within the first 5 d after application (Fig. 2). These results are similar to those of previous studies that the considerable rate of rotenone decays in the field on the order of days (Cabras et al., 2002; Zhou et al., 2013). Although the initial concentrations of WDG in cabbage and soil were higher than those of SC, the half-lives of the two formulations exhibited no difference. The initial concentrations of WDG in cabbage were 1.2040, 1.0134, and 1.7479 mg $kg^{-1}$ with half-lives of 1.96, 1.33, and 1.72 d, respectively. The initial concentrations of SC were 0.7587, 0.7312, and 0.8776 mg $kg^{-1}$ with half-lives of 1.14, 1.52, and 1.85 d, respectively (Table 1). Correspondingly, the initial concentrations of WDG in soil were 0.1417, 0.1519,

**Table 1**
Half-lives and regression equations of the SC and WDG formulations of rotenone in cabbage.

| Formulation | Experimental sites | Regression equation | Correlation coefficient ($R^2$) | Half-life (d) |
|---|---|---|---|---|
| 2.5 percent SC | GZ | $C=0.6126e^{-0.609T}$ | 0.9261 | 1.14 |
| | QJ | $C=0.4363e^{-0.457T}$ | 0.9075 | 1.52 |
| | NN | $C=0.5783e^{-0.375T}$ | 0.8847 | 1.85 |
| 3 percent WDG | GZ | $C=0.5781e^{-0.354T}$ | 0.8412 | 1.96 |
| | QJ | $C=1.0981e^{-0.520T}$ | 0.9663 | 1.33 |
| | NN | $C=1.5503e^{-0.402T}$ | 0.9861 | 1.72 |

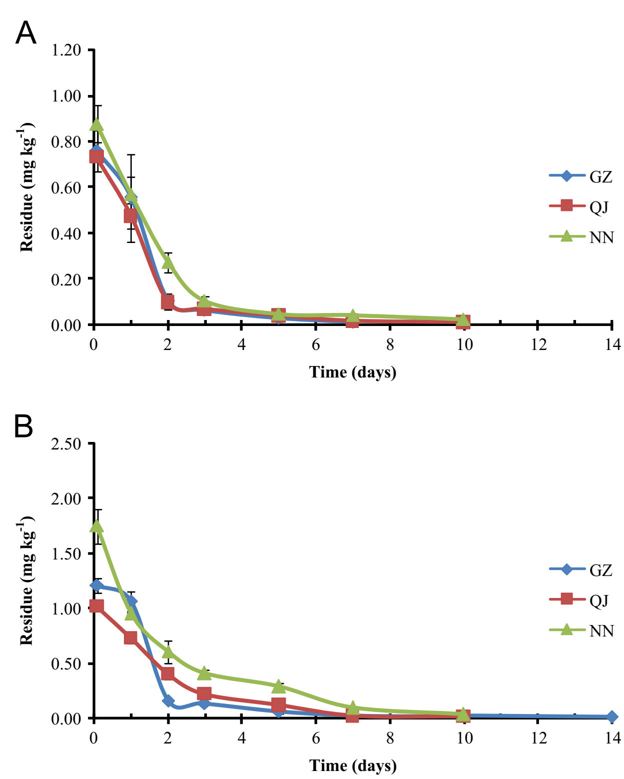


**Fig. 1.** Decline curves of the SC and WDG formulations of rotenone in cabbage under three agro climatic zones in China (A: 2.5 percent SC and B: 3 percent WDG).