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Dissipation and Residue of Cyprodinil in Strawberry and Soil

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Abstract The dissipation of cyprodinil under field and greenhouse condition in China was investigated. The pesticide cyprodinil dissipation differed under different cultivate conditions, the half lives were 14.5 and 12.5 days in strawberry and soil, respectively, under the field condition, 5.5 and 6.5 days, respectively, under greenhouse. The results showed that the dissipation rate under greenhouse condition was much faster than under field condition either in strawberry or soil. The terminal residues in strawberries were below the EU maximum residue level (5 mg/kg) after 7 days of application. This study will give a suggestion for the reasonable use of cyprodinil under different cultivate conditions and can also provide reference to set MRL value in strawberry in China.

Keywords Cyprodinil · Dissipation · Strawberry · Soil · Field · Greenhouse

Strawberry is widely cultivated for its delicious juicy flesh and its high nutritive value. It's also well known for the medicinal properties and health care, and it is represented as the queen of fruit. Strawberry is also a popular raw material for the food industry, for examples, the fresh fruits can be made into many kinds of fruit preparations as ingredients for yogurts, milk, ice cream or in the candy industry. The juice or concentrates are used in multi-fruit-based juices or beverages and for the production of liqueurs, fruit wines (Will and Krüger 1999).

However, there are many diseases occur during the growth of strawberry, such as grey mould, rusts and mildews. Those diseases decrease seriously the quality and output of strawberries. Therefore, the applications of some fungicides including cyprodinil were essential.

Cyprodinil (4-cyclopropyl-6-methyl-N-phenylpyrimidin-2-amine, Fig. 1) is a pyrimidinamine fungicide which developed and introduced by Novartis Crop Protection AG and first marketed in 1994 (Pesticide manual, V2.0). Previous researches were mainly concentrated on the analytical method of cyprodinil. For example, Pan et al. (2009) analyzed the cyprodinil residue in grape using gas chromatography (GC), Vaquero-Fernández et al. (2008) described a liquid chromatography (LC) method to analyze cyprodinil and fludioxonil in model solutions of must and wine, GC coupled with mass spectrometry and HPLC coupled with mass spectrometry were also introduced to determine cyprodinil (Patil et al.2009; Romero-Gonzalez et al. 2008). However, few researches were on the dissipation of cyprodinil under field condition. Cabizza et al. (2007) studied the degradation of cypordinil on lettuce, and found that both distribution methods and lettuce cultivar affect the degradation trends of cyprodinil.

In China, the strawberry usually cultivates under two different conditions, including field and greenhouse. So far as our evidence goes, there was no report on the dissipation of cyprodinil in strawberry. The objective of this study was to investigate the dissipation and residue of cyprodinil in strawberry and soil under field and greenhouse condition.

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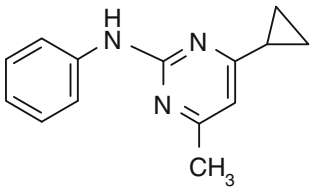
Fig. 1 The chemical structure of cyprodinil



Materials and Methods

Cypridinil standard with purity of 99.0% was obtained from Standard Technology Development (Beijing, China); HPLC-grade acetonitrile and methanol were from Fisher Scientific International Inc. USA. Anhydrous magnesium sulfate and sodium chloride were purchased from Beijing Chemical Reagent Co. Ltd., China. High speed centrifuge (RJ-TDL-40B) was from Beijing Medicine Centrifuge Factory, China.

The field trial was conducted in Beijing under field and greenhouse condition. The application of cyprodinil (50%WG) was in the dosage of 1,080 g.a.i.ha^{-1} (gram of active gradient per hectare) to investigate the dissipation of cyprodinil. Different treatments and control plot were 30 m^2 and the buffer zone was set up between plots. Each treatment was with three replicates. The samples were collected on day 0, 1, 3, 5, 7, 10, 14 and 21 days after application. The strawberry samples were homogenized by a blender after removal of stem then stored at −20°C. The soil samples were homogenized after removal of stone and leaves, then stored at −20°C.

The terminal residue experiment was performed at the recommended dosage level of 720 g.a.i.ha^{-1}. It was applied 3 times with an application interval of 7 days with 3 replicates. Representative strawberry and soil samples were then collected 7 days after the last application of cyprodinil.

Ten grams of sample was weighed into a 50 mL Teflon centrifuge tube, and mixed by vortexing for 1 min after adding 10 mL acetonitrile. Then 4 g anhydrous magnesium sulfate and 1 g sodium chloride were added. The sample was mixed further by vortexing for 1 min and centrifuged for 10 min at 3,800 r min^{-1}. One milliliter supernatant was filtered through a 0.22 μm filter membrane and transferred into the autosampler vial for HPLC analysis.

A Lumtech series liquid chromatography system with a diode array detector (DAD) was used to analyze the concentration of cyprodinil residue. Xcalibur software was used for data acquisition. Analysis was performed on a C18 column (5 μm particle size, 150 mm × 4.6 mm id, Agilent Company, USA). The mobile phase was water and methanol (V/V = 30:70) with a flow rate of 1 mL/min when the soil sample was analyzed. The chromatographic conditions were as follows when strawberry was analyzed: eluent A, water; eluent B, methanol; flow rate, 1 mL/min; gradient, 60% B in the first 1 min, and then 60–70% B over the next 14 min, then was stable for 5 min, each running time was 20 min. The injection volume was 20 μL. The detection wavelength was 269 nm.

Results and Discussion

Six different concentrations of strawberry and soil matrix standards (0.02, 0.05, 0.1, 0.5, 1.0 and 2.0 mg/kg) of cyprodinil were prepared to determine the linearity. Good results were showed with a correlation coefficient of 0.999 in strawberry and 0.998 in soil, respectively. Standard of cyprodinil were spiked to the strawberry and soil samples at three different levels (0.1, 0.5 and 1.0 mg/kg) to evaluate the efficiency of the method, each level was repeated 3 times. The average recoveries were found from 84.84% to 94.21% in strawberry with a relative standard deviation (RSD) from 1.46% to 2.14%, from 83.16% to 107.43% in soil with RSD from 3.01% to 4.33%, respectively. The limit of detection (LOD) of cyprodinil was set at a signal to noise ratio of 3:1, and the results are shown in Table 1.

The dissipation trend of cyprodinil was determined by plotting residue concentration over time. The results are shown in Figs. 2 and 3. From the figures, the dissipation half lives of cyprodinil in strawberry and soil under field and greenhouse condition were obtained.

It can be seen from the results that the half lives of cyprodinil in strawberry and soil under field condition were 14.5 and 12.5 days, respectively. The half lives of cyprodinil under greenhouse condition were 5.5 and 6.5 days in strawberry and soil, which was much faster than under the field condition. The results indicated that the pesticide cyprodinil degrades faster under greenhouse condition than field condition either in strawberry or soil. It was explained by the difference of the field and greenhouse condition. The temperature and humidity were at almost fixed level (temperature of 25–30°C and humidity of 70–80% according to the experimental record), however, the weather conditions in field were mutable, such as the temperature, the precipitation, the wind direction and velocity. So there was no drift of pesticide or diurnal change of temperature or humidity in the greenhouse compared with filed condition. The initial residue of cyprodinil in strawberry and soil under field condition was much lower than greenhouse (1.97 and 0.62 mg/kg in strawberry and soil under field condition, while 15.03 and 11.19 mg/kg under greenhouse condition). The plant coverage degree and fruit setting of strawberry under greenhouse condition were much higher than under field condition. Maybe this is the reason why the initial residue of cyprodinil was different.

Table 1 The fortified recovery of cyprodinil in strawberry and soil sample (n = 3)

Spiking level (mg/kg)	Strawberry		LOD (mg/kg)	Soil		LOD (mg/kg)
	Average	RSD (%)		Average	RSD (%)	
0.1	84.84	2.14	0.03	83.16	3.40	0.03
0.5	95.36	1.67		87.97	3.01	
1.0	94.21	1.46		107.43	4.33	

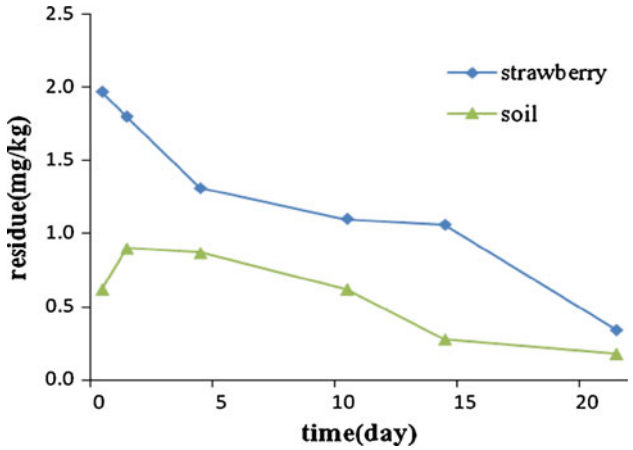


Fig. 2 The dissipation of cyprodinil in strawberry and soil under field condition

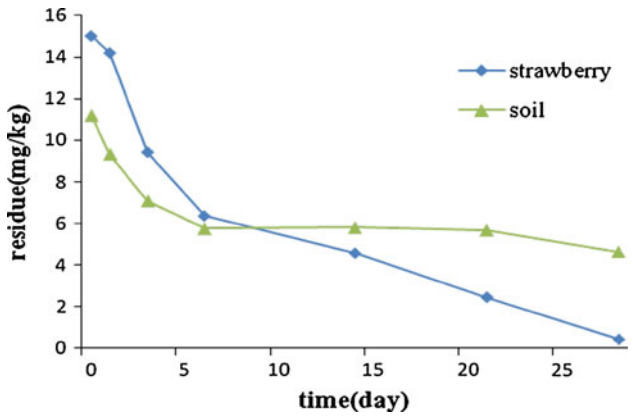


Fig. 3 The dissipation of cyprodinil in strawberry and soil under greenhouse condition

The terminal residue of cyprodinil after pre-harvest interval (PHI) of 7 days in strawberry of field and greenhouse conditions were 2.84 mg/kg and 4.57 mg/kg, respectively. The residues in soil of field and greenhouse conditions were 0.47 mg/kg and 13.38 mg/kg, respectively. It can be seen that the residues of cyprodinil in strawberry were lower than the EU maximum residue limit (MRL) of 5 mg/kg (https://secure.pesticides.gov.uk/MRLs/). For the lower dissipation rate, it could give us a reminder that when the pesticide cyprodinil (50% WG) was used in greenhouse strawberry, the dosage of application and harvest interval should be controlled in order to make it safer. For example, the application dosage of cyprodinil should not be increased, or the harvest interval should be extended, or to make a mixture of pesticide, such as cyprodinil + fludioxonil, which was already used in strawberry to protected the disease (Walter et al. 2005 and Wedge et al. 2007), and this needs further research.

To sum up, the dissipation of cyprodinil in strawberry and soil under field and greenhouse condition in China was investigated. The result will give a suggestion of reasonable and safe use of the pesticide cyprodinil, and can also provide reference to set MRL value in strawberry in China.

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