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Residues of cyantraniliprole and its metabolite J9Z38 in rice field ecosystem

Changpeng Zhang [1], Xiuqing Hu [1], Hua Zhao, Min Wu, Hongmei He, Chunrong Zhang, Tao Tang, Lifeng Ping, Zhen Li *

State Key Lab Breeding Base for Zhejiang Sustainable Plant Pest Control, MOA Key Lab for Pesticide Residue Detection, Institute of Quality and Standard for Agro-Products, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, China

HIGHLIGHTS

- A method was developed to detect of cyantraniliprole and J9Z38 in rice.
- The half-lives of cyantraniliprole were 3.2, 4.4 and 6.3 d in rice straw, respectively.
- The recommended MRL of cyantraniliprole was 0.1 mg kg^{-1} in brown rice.

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ABSTRACT

A simple and reliable analytical method was developed to detect cyantraniliprole (HGW86) and its metabolite J9Z38 in rice straw, paddy water, brown rice, and paddy soil. The fate of cyantraniliprole and its metabolite J9Z38 in rice field ecosystem was also studied. The target compounds were extracted using acetonitrile, cleaned up on silicagel or strong anion exchange column, and analyzed by ultra-performance liquid chromatography–tandem mass spectrometry. The average recoveries of cyantraniliprole and J9Z38 in rice straw, paddy water, brown rice, and paddy soil ranged from 79.0% to 108.6%, with relative standard deviations of 1.1–10.6%. The limits of quantification of cyantraniliprole and J9Z38 were 18 and 39 μg kg^{-1} for rice straw, 2.8 and 5.0 μg kg^{-1} for paddy water, 4.3 and 6.3 μg kg^{-1} for brown rice, and 3.9 and 5.3 μg kg^{-1} for paddy soil. The trial results showed that the half-lives of cyantraniliprole were 3.2, 4.4, and 6.3 d in rice straw and 4.9, 2.0, and 6.2 d in paddy water in Zhejiang, Hunan, and Shandong, respectively. The respective final residues of cyantraniliprole and J9Z38 in brown rice were lower than 0.05 and 0.02 mg kg^{-1} after 14 d of pre-harvest interval. The maximum residue limit of cyantraniliprole at 0.1 mg kg^{-1} and dosage of 100 g a.i. hm^{-2}, which could be considered safe to human beings and animals, were recommended.

1. Introduction

Cyantraniliprole (3-bromo-N-[4-cyano-2-methyl-6-[(methylamino)-hydroxy]phenyl]-1-(3-chloro-pyridine-2-yl)-1-H-pyridine-5-formamide, DPX-HGW86) is an o-amino-benzamide insecticide in which a cyano group replaced the 4-halo substituent of the former anthranilic diamide chlorantraniliprole (Feng et al., 2010). The mode of action of cyantraniliprole relies on the activation of the ryanodine receptors of insects, which are critical for muscle contraction (Lahm et al., 2007). This activation of the ryanodine receptors affects calcium homeostasis by unregulating the release of internal calcium in the cell, which leads to feeding cessation, lethargy, muscle paralysis, and ultimately, death of the insect (Cordova et al., 2006; Jacobson and Kennedy, 2011). Cyantraniliprole exhibits remarkable selectivity and low toxicity to mammals, improved plant mobility and increased spectrum has been reported (Lahm et al., 2009; Dong et al., 2012). Cyantraniliprole is used to control Lepidoptera pests and sucking pests in a wide range of crops (Chai et al., 2012).

Studies on analytical methods for cyantraniliprole residue have been reported in several crops, vegetables, and environmental materials (Schwarz et al., 2011; Sergio et al., 2011; Timo et al., 2011; Dong et al., 2012; Sun et al., 2012). However, to our knowledge, a residue analytical method for cyantraniliprole and its metabolite J9Z38 in rice has not been reported to date. Moreover, the maximum residue limits (MRLs) of cyantraniliprole in rice have not been legislated in America, European Union, or China. No study has been reported on the fate of cyantraniliprole in rice field ecosystems.

Improper and extensive use of pesticides does not only pollute cultivated soil and groundwater, but it also accumulates in aquatic plants (Jiries et al., 2002; Yu and Zhou, 2005). Public concern over

* Corresponding author. Tel.: +86 571 86404056; fax: +86 571 86402186.
E-mail addresses: lz20010@163.com, cpzhang1215@126.com (Z. Li).
[1] These authors equally contributed to this work.

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pesticide residues in food has become important in food safety. In this work, a simple ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) method was established to detect residues of cyantraniliprole and its metabolite J9Z38 in rice straw, paddy water, brown rice, and paddy soil. In addition, a field study was performed to investigate the fate of cyantraniliprole in a rice field ecosystem. This work would help the government establish the MRL of cyantraniliprole in rice and provide basic information for proper use of cyantraniliprole in pest management strategies in rice fields to protect public health.

2. Materials and methods

2.1. Materials and reagents

The cyantraniliprole standard (purity, 99.2%), J9Z38 standard (purity, 97.2%), and commercial formulation (10% oil suspension) were obtained from DuPont company (USA). Acetonitrile (chromatography grade) was supplied by Burdick & Jackson (Ulsan, Korea). Analytical grade acetonitrile, formic acid, and ammonium formate were purchased from Shanghai Lingfeng Chemical Regent Co., Ltd. (Shanghai, China). Silica gel columns (500 mg/3 mL) and strong anion exchange (SAX) columns (500 mg/6 mL) were purchased from Agela Technologies (Tianjin, China).

The properties of cyantraniliprole and J9Z38 are presented in Table 1. Standard stock solutions of cyantraniliprole (1000 mg L^{-1}) and J9Z38 (1000 mg L^{-1}) were prepared in acetonitrile. The standard stock solution of cyantraniliprole/J9Z38 (10.0/20.0 mg L^{-1}) was then obtained through dilution with acetonitrile. The standard solutions required to construct a calibration graph (0.5/1, 1/2, 5/10, 10/20, 50/100, and 100/200 μg L^{-1}) were prepared from the stock solution through serial dilution with acetonitrile. All solutions were stored in a refrigerator in the dark at 4 °C. Observation for 3 months showed no degradation in the working standard solutions.

2.2. Field experiment

Field experiment site A was at Yangdu Village, which is located in Haining town, Hangzhou City, Zhejiang Province, PR China. The soil organic matter content and pH of site A were 12.3 g kg^{-1} and 7.1, respectively. Field experiment site B was at the experimental plot of Hunan Agricultural University in Changsha City, Hunan Province. The soil organic matter content and pH of site B were 1.2 g kg^{-1} and 7.8, respectively. Field experiment site C was at Yaxin Village, which is located in Licheng town, Jinan City, Shandong Province. The soil organic matter content and pH of site C were 21.8 g kg^{-1} and 6.1, respectively. The kinetic study was carried out in six field plots, each with an area of 30 m^2. The area was divided by irrigation and drainage channels. Cyantraniliprole formulations (10% oil suspension) were sprayed at 150 g a.i. hm^{-2} (1.5 times of the recommended dose), and the untreated plots were sprayed with water as control. Each experiment was conducted in triplicate. The representative samples were collected at 1 h, 3, 5, 7, 14, 21, 28, 35, 42, and 60 d (rice straw, paddy water, and paddy soil) after cyantraniliprole application. Rice straw samples (1.0 kg) were cut into pieces, mixed fully, and collected randomly in each treatment. Paddy water samples (500 mL) were collected randomly in each treatment. Paddy soil samples (1.0 kg) from the top (0 cm) to 15 cm were collected and mixed fully in each treatment. The samples were placed in a freezer at −20 °C until analysis.

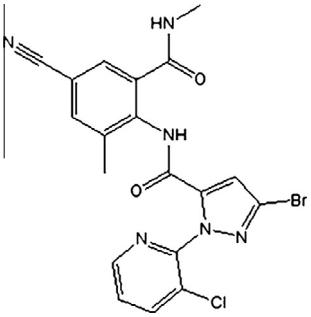
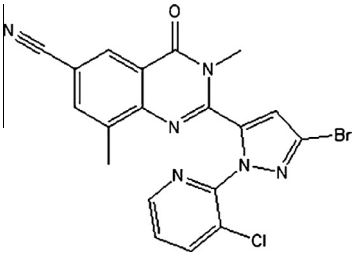
The ultimate residue field test was carried out in 12 field plots, each with an area of 30 m^2. Cyantraniliprole formulations were sprayed at two doses, 100 g a.i. hm^{-2} (recommended) and 150 g a.i. hm^{-2} (1.5 times of the recommended). The treated plots were sprayed two or three times for each dose at 7 d intervals. The untreated plots were sprayed with water as control. Each experiment was conducted in triplicate. The samples (rice straw, brown rice, and paddy soil) were collected at intervals of 7, 14, and 21 d after the last spray. Brown rice samples were acquired by removing the husk of rice. The collected samples were placed in a freezer at −20 °C until analysis.

2.3. Sample preparation

2.3.1. Rice straw

Approximately 2.0 g of sample (dried rice straw) was weighed into a 150-mL conical flask. Acetonitrile (30 mL) and water (10 mL) were added. The mixtures were shaken vigorously for 0.5 h and then filtered. A total of 15 mL of acetonitrile was added

Table 1
Properties and MS/MS parameters for cyantraniliprole and J9Z38.

Compound	Cyantraniliprole	J9Z38
Molecular formula	$C_{19}H_{14}BrClN_6O_2$	$C_{19}H_{12}BrClN_6O$
Molecular weight	475	457
log Pow (22 °C)	1.94	/
Water solubility (mg/L, 20 °C)	14.24	/
Acute toxicity of rats	Slightly toxic	/
Cone voltage (V)	20	50
Quantification ion transition	475 → 286	457 → 188
CE1 (eV)	20	30
Qualitative ion transition	475 → 444	457 → 299
CE2 (eV)	20	35
Structure		

CE, collision energy.