Ecotoxicology and Environmental Safety 80 (2012) 252–257

Contents lists available at SciVerse ScienceDirect

Ecotoxicology and Environmental Safety

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

Dissipation of pyraclostrobin and its metabolite BF-500-3 in maize under field conditions

Xiangwei you[a], Congyun liu[a,b], Fengmao liu[a,*], Yanping liu[a,c], Jiannan dong[a]

[a] College of Science, China Agricultural University, Beijing 100193, PR China
[b] Research Center for Quality Safety and Standard of Agricultural Products, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, PR China
[c] Plant Protection Research Institute, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, PR China

ARTICLE INFO

Article history:
Received 3 December 2011
Received in revised form
9 March 2012
Accepted 14 March 2012
Available online 19 April 2012

Keywords:
Pyraclostrobin
Metabolite
HPLC-MS/MS
Residue

ABSTRACT

The dissipation and residue of pyraclostrobin and its metabolite BF-500-3 in maize under field conditions were investigated. A sensitive, simple and fast method for simultaneous determination of pyraclostrobin and BF-500-3 in maize matrix was established by high performance liquid chromatography–tandem mass spectrometry (HPLC-MS/MS). The average recoveries of pyraclostrobin and BF-500-3 were found in the range of 83.6–104.9% with relative standard deviations (RSDs) of 2.3–10.0%. The results showed that pyraclostrobin dissipated quickly in maize plant with half-lives of 1.6–1.7 days. Its metabolite BF-500-3 showed a tendency of rapid increasing initially and decreasing afterwards. At harvest time, the terminal residues of pyraclostrobin were below the maximum residue limit (MRL) set by USA and Canada in maize grain when measured 7 days after the final application, which suggested that the use of this fungicide was safe for humans. The results could provide guidance to safe and reasonable use of pyraclostrobin in agriculture.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Maize (*Zea mays*) is an important grain crop for its heavy consumption, high nutritional value, economic value and medicinal value (Zhao et al., 2010). Pesticide applications were essential to protect maize from pests including fungi.

Pyraclostrobin (methyl2-[1-(4-chlorophenyl) pyrazol-3-yloxymethyl]-*N*-methoxycarbanilate) is a novel strobilurin fungicide and was discovered by BASF in 2000. Alone or in combination with other fungicides, pyraclostrobin is able to protect grapes, strawberries, peppers, tomatoes, and cereals from fungal diseases (Esteve-Turrillas et al., 2011; González-Rodríguez et al., 2009a, 2009b, 2011). It is also applied on maize to prevent northern corn leaf blight caused by *Setosphaeria turcica* infestation. In 2004, the use of pyraclostrobin was accepted in the European Union, so it was included in Annex I of Directive 91/414/EEC, and by the end of 2005, it had been approved in more than 50 countries for over 100 crops in over 100 indications (Mercader et al., 2008). Because of the wide application, residue of pyraclostrobin in different agro-products was detected. In a recent report published by the European Food Safety Authority (EFSA), residues of pyraclostrobin were detected in 3.8% of the fruit and vegetable surveillance samples analyzed in the 27 EU Member States, Norway and Iceland (Esteve-Turrillas et al., 2011). The desmethoxy metabolite of pyraclostrobin BF-500-3 (methyl-*N*-[[[1-(4-chlorophenyl)-pyrazol-3-yl]oxy]-*o*-tolyl]-carbamate) was assumed to be of similar toxicity to pyraclostrobin (http://www.epa.gov/pesticides/chem_search/cleared_reviews/csr_PC-099100_9-Oct-01_a.pdf). So the residue of pyraclostrobin in crops was defined as the sum of parent pyraclostrobin and its desmethoxy metabolite BF-500-3, calculated as the stoichiometric equivalent of pyraclostrobin in the USA and Canada (http://www.mrldatabase.com/; http://www.hc-sc.gc.ca/cps-spc/pest/part/protect-proteger/food-nourriture/mrl-lmr-eng.php). Fig. 1 shows the chemical structure of pyraclostrobin and BF-500-3.

The analytical methods of pyraclostrobin residues were described in some previous literatures. At present, the pyraclostrobin residue analysis is mainly performed via gas Chromatography (GC) (Hirahara et al., 2005; Wang et al., 2010), high performance liquid chromatography (HPLC) (de Melo Abreu et al., 2006), GC coupled with mass spectrometry (GC–MS) (dos Santos and Pereira, 2010; González-Rodríguez et al., 2009a, 2009b, 2011; Viñas et al., 2009), HPLC coupled with tandem mass spectrometry (HPLC-MS/MS)(Anagnostopoulos et al., 2009; Hetherton et al., 2004; Lesueur et al., 2008) and ELISA (Esteve-Turrillas et al., 2011). But the method of BF-500-3 residue analysis was not reported.

There were few studies on the dissipation of pyraclostrobin under field condition. Li et al., (2010) revealed that the half-life of pyraclostrobin in grape was 3.7–3.8 days. Zhang et al., (2009) reported that the half-life of pyraclostrobin in greenhouse

---

[*] Corresponding author. Fax: +86 10 62733620.
E-mail address: liufengmao@cau.edu.cn (F. liu).

0147-6513/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.ecoenv.2012.03.012

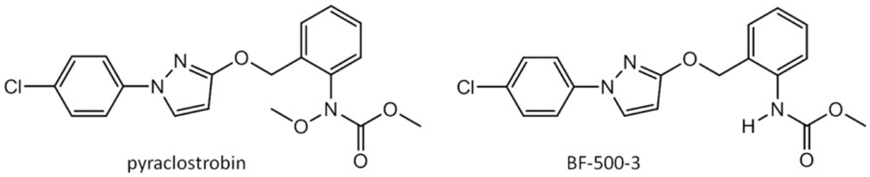

Fig. 1. Chemical structures of pyraclostrobin and BF-500-3.

strawberry was 3.39–4.06 days. However, the metabolite BF-500-3 was ignored in those dissipation studies.

In this study, we established a simple simultaneous analytical method for pyraclostrobin and BF-500-3 in maize and evaluated the residue levels and dissipation of pyraclostrobin and BF-500-3 residues in China. The results will be helpful to establish MRL of pyraclostrobin in maize and provide guidance for proper and safe use of this fungicide.

2. Materials and methods

2.1. Materials and reagents

Pyraclostrobin standard was purchased from Agricultural Environmental Protection Institution in Tianjin, China, with the purity 99.6%; BF-500-3 standard was supplied from Guangdong Academy of Agricultural Science, with the purity 99.7%. HPLC grade acetonitrile was purchased from Honeywell (Burdick & Jackson). Graphitized carbon black (GCB), octadecylsilane (C_{18}) and primary secondary amine (PSA) were from Bonna-Agela Technologies, Ltd. Neutral alumina and florisil were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium chloride and anhydrous magnesium sulfate were purchased from Beijing Chemical Reagents Company, China.

2.2. Field experiment design

The experiment was conducted in Beijing (E116.46, N39.92) and Shandong (E117.01, N36.65) in the year 2010 according to “The guideline for Pesticide Residue Field Experiment” issued by the Ministry of Agriculture, People’s Republic of China (NY/T 788–2004). Each treatment consisted of three replicate plots and a control plot. The area of each plot was 5×6 (30) m^2, and 1 m distance was used as a buffer area to separate each plot in the same field.

In order to investigate the dissipation of pyraclostrobin in maize plant, pyraclostrobin formulation (250 g/L of EC) were sprayed at a dosage of 421.8 ga.i./ha (gram of active ingredient per hectare) (1.5 times of the recommended dose) in the experiment plots when the maize plant was at 8–10 leaf stage.

In order to investigate the terminal residue of pyraclostrobin in maize, the recommended dosage (281.25 ga.i./ha with two treatments: spray 3 times and 4 times and with two harvest intervals: 7, 10 days) were conducted in two plots, separately. There was a 7 days interval between two applications.

2.3. Sampling and storage

Representative samples were collected at random from each plot at different time intervals.

To investigate the dissipation of pyraclostrobin, the maize plant samples were collected 2 h, 12 h, 1, 3, 5, 7 days after spraying. To determine the terminal residue of pyraclostrobin, Both maize grain and maize plant samples were collected at the harvest time (7 and 10 days after the last spraying).

All the samples were homogenized and stored at -20 °C prior to analysis.

2.4. Sample extraction and clean-up

Previously homogenized sample of maize plant (4 g) or maize (5 g) was weighed into a centrifuge tube and 20 mL acetonitrile was added. Then the sample was shaken in an air bath oscillator for about 1 h. After addition of 2 g anhydrous magnesium sulfate and 1 g sodium chloride, the sample was shaken vigorously for 1 min and centrifuged for 5 min at 3800 rpm.

Then, a volume of 1 mL acetonitrile layer was transferred into another 2 mL centrifuge vial containing 50 mg of C_{18}. The sample was mixed vigorously on a vortex mixer for 1 min and then centrifuged for 2 min at 6000 rpm. Prior to injection into the HPLC-MS/MS system, the sample was filtered through a 0.22 μm filter.

2.5. HPLC/MS/MS conditions

The HPLC-MS/MS system from Agilent Technologies consisted of a 1200 Series liquid chromatography pump coupled to a triple quadrupole mass spectrometer (6410 Triple Quad). A ZORBAX Eclipse XDB C_{18} column, 1.8 μm, 2.1×50 mm (Agilent) was used for the separation of fungicides. The isocratic mobile phases, which were composed of methonal and water (90:10) was pumped at a flow rate of 300 μL/min. The injection volume was 5 μL.

The HPLC-MS/MS was performed in the multiple-reaction monitoring (MRM) mode and the positive ESI mode. The gas temperature was set at 350 °C with the gas flow (N_2) at 8 L/min, the nebulizer pressure was 35 psi. The fragmentor voltages for pyraclostrobin and BF-500-3 were 120 and 90 V, respectively. The MRM transitions for pyraclostrobin were m/z 388 → 194 (collision energy, 10 eV), 388 → 163 (collision energy, 20 eV), and for BF-500–3 358 → 164 (collision energy, 7 eV), 358 → 132 (collision energy, 29 eV). A single MRM was used to perform quantification and the quantitative MRM transitions for pyraclostrobin and BF-500-3 were m/z 388 → 194 and 358 → 132, respectively.

2.6. Calculation

The concentration and half-life of pyraclostrobin residue were calculated by the first-order kinetics equations $C_T=C_0e^{-KT}$ and $T_{1/2}=\ln2/K$, respectively. Where T is the time (in days) after pesticide application, C_T is the residue concentration at time T, C_0 is the initial concentration after application (at $T=0$), K is the dissipation coefficient, and $T_{1/2}$ is the half-life of pyraclostrobin dissipation.

3. Results

3.1. Method validation

3.1.1. Optimization of mass spectrometry

For the similar chemical structures, pyraclostrobin and BF-500-3 have similar physical and chemical properties. They were not separated well after eluting the column with the mobile phase in an isocratic mode. However, in the full-scan mass spectrometry of pyraclostrobin and its product ion mass spectrometry of $[M+H]^+$ ion (Fig. 2), the $[M+H]^+$ ion of BF-500-3(m/z 358), which was chosen as the precursor ion, was not found. Therefore, it could be assumed that pyraclostrobin and BF-500-3 would not interfere with each other in the MS analysis, even though they had the same retention time. This will avoid the extra time caused by gradient elution.

3.1.2. Optimization of adsorbents in clean-up

Dispersive solid phase extraction (DSPE) method was selected in clean-up procedure. Different type and amount of adsorbents were compared including PSA, GCB, neutral alumina, C_{18} and florisil. The results showed that the adsorbent affected not only the response value of pyraclostrobin and BF-500-3 but also the shape of the peaks. C_{18} showed the better clean-up results for both pyraclostrobin and BF-500-3 in maize plant matrix (Fig. 3) and in maize grain matrix. Further, clean-up with different amount of C_{18} (30, 40, 50 mg for maize grain and 10, 30, 40, 50 mg for maize plant, respectively) was evaluated. The response value of pyraclostrobin and BF-500-3 increased in the maize plant matrix with the increase of the amount of C_{18} (Fig. 4). In the maize grain matrix, both 40 and 50 mg of C_{18} gave satisfactory results, but the extract of maize grain with 50 mg of C_{18} was more

Download English Version:

https://daneshyari.com/en/article/4420690

Download Persian Version:

https://daneshyari.com/article/4420690

Daneshyari.com