Bull Environ Contam Toxicol (2007) 79:445–447
DOI 10.1007/s00128-007-9262-z

Dissipation and Residues of Carfentrazone-ethyl in Wheat and Soil

Lijun Han · Yanjun Xu · Maofeng Dong · Chuanfan Qian

Received: 10 April 2007 / Accepted: 25 July 2007 / Published online: 23 August 2007

Abstract The purpose of this article was to study the dissipation rate of carfentrazone-ethyl in soil and its terminal residue in wheat field eco-system. The results showed that carfentrazone-ethyl dissipated rapidly in soil after application. Its half-lives in soil were 5.8 and 3.8 h in Beijing and Jilin, respectively. The terminal residues of carfentrazone-ethyl in soil samples were very low (around 0.003–0.005 mg/kg), and the residues in wheat grain were not detectable. The use of carfentrazone-ethyl in wheat could be considered to be safe.

Keywords Dissipation · Residue · Carfentrazone-ethyl · Wheat

Carfentrazone-ethyl is a triazolinone herbicide developed by FMC Corporation. It is mainly used in wheat, maize, soybeans, cotton, grain sorghum, sweet corn, oats, barley, rice and turf fields to kill kargeleaf, ruderal and sedge. Carfentrazone-ethyl is a post-emergence herbicide to control weeds through the process of membrane disruption which is initiated from the inhibition of the enzyme protoporphyrinogen oxidase. In plants, the inhibition interferes with the chlorophyll biosynthetic pathway. In mammals, this inhibition interferes with the heme biosynthetic pathway. Based upon a battery of acute toxicity studies, Carfentrazone-ethyl is classified as toxicity categories III and IV (USEPA 1998) and is considered to be practically non-toxic to birds, but it is moderately toxic to aquatic animals.

L. Han (✉) · Y. Xu · M. Dong · C. Qian
Department of Applied Chemistry, China Agricultural University, Beijing 100094, China
e-mail: hlj2000@cau.edu.cn; hanlijun2000@163.com

Since its introduction to China in 2000, Carfentrazone-ethyl has been applied to many kinds of crops, including wheat, maize, soybeans, cotton and rice. Wheat is a widely cultivated crop in China, which is produced in two growth seasons. Kargeleaf, ruderal and sedge are very common harmful weeds in the wheat fields in China, and caused seriously damage to the wheat production. Recent studies showed that carfentrazone-ethyl would be a valuable alternative herbicide against the broadleaf weeds, especially for the resistant weeds in the fields with long-term use of the sulfonylurea herbicides (Liu et al. 2000).

As it is a relatively novel herbicide, there were few research reports about the residue and degradation of carfentrazone-ethyl. Dayan et al. (1997) investigated the selectivity and the mode of action of carfentrazone-ethyl in soybean and in weeds using the radioactive methodology. Also using the radioactive method, another group (Thompson and Nissen 2000) reported the absorption and degradation of carfentrazone-ethyl in soybean, maize and *Abutilon Theophrastus*. Their results showed that carfentrazone-ethyl broke down rapidly in soybean and maize, but it degradated slower in *Abutilon Theophrastus*.

The purpose of this article was to study the dissipation rate of carfentrazone-ethyl in soil and its terminal residue in wheat field eco-system in order to provide a guideline for the scientific and safe use of carfentrazone-ethyl.

Materials and Methods

The analytical standards of Carfentrazone-ethyl (90.1%) and the Affinity 40DF formulations (40 g a.i./100 g) were obtained from FMC Corporation, USA. Chromatography grade *n*-hexane and ethyl-acetate were supplied from Tedia (Fairfield, OH, USA). Analytical grade petroleum ether, acetone, anhydrous sodium sulfate, florisil and activated carbon absorbent were purchased form Beijing Reagent Company (Beijing, China).

All analysis was conducted with Agilent 6890 mode GC equipped with electron capture detection (ECD) (Agilent, USA). An OV-1701 fused silica capillary column (15m × 0.53mm i.d.) was used as separation column; temperatures were set as: injector 230°C; column oven 210°C; detector 250°C; the carrier gas was N_2 with a flow rate of 2 mL/min. The retention time of carfentrazone-ethyl was 14 min.

The field trials including the dissipation experiments and terminal residue experiments were carried out in Jilin (located in the north-east of China) and Beijing, China. Each experiment field contained three replicate plots and a control plot which was separated by irrigation channels, and the area of each plot was 30 m^2.

Affinity 40DF was sprayed in the wheat field after the emergence of the first two leaves of the broadleaf weeds. The dose of application was 120 g/hm^2 (two times of the recommended dosage) in Beijing. Because the residue of carfentrazone-ethyl was very low in Beijing, the dose in Jilin was set as 600 g/hm^2. Representative soil samples were collected about 1, 2, 4, 6, 8, 12, 24, 48 and 72 h after spraying. All the collected samples were stored in a freezer at –20°C for further analysis.

The terminal residue experiments were carried out with a dosage level 60 g/hm^2 (recommended dosage) and a higher dosage level 120 g/hm^2 (two times of the recommended dosage), respectively. After the emergence of two leaves of the broadleaf weeds in the wheat field, the treatment was conducted, and then representative wheat grains and soil samples were collected 3 days before harvest of the wheat. The wheat grains were grinded to 60–80 mesh with a cereal grinder. The samples were stored in a freezer at –20°C for analysis.

Twenty grams of soil or 10 g wheat sample was put in a 250-mL flask. Carfentrazone-ethyl was extracted by adding 50 mL acetone:water (80:20), and the mixture was shaken on a reciprocating shaker for 30 min. The samples were filtered through a Whatman number 1 filter paper in a Büchner funnel into a 250-mL side-arm flask under vacuum, and were washed twice with 10 mL acetone. After that, the filtrate was evaporated to eliminate most of the acetone. The rest of the extracts were transferred into a 250-mL separatory funnel for liquid–liquid extraction (LLE).

About 30 mL of 10% sodium chloride solution was added to the separatory funnel, and the analyte was extracted with 30, 20, 20 mL petroleum ether subsequently by vigorously shaking for about 30 s. The organic layer was collected in a 250-mL flask and evaporated to dryness using the rotary vacuum evaporator at 45–50°C. The residue in flask was dissolved in 5 mL hexane for further clean-up by column chromatography.

Table 1 Fortified recovery of carfentrazone-ethyl in wheat and soil sample

Sample (g)	Spiked amount (μg)	Spiked concentration (mg/kg)	Average recovery ± SD[a] (%)	RSD (%)
Wheat (10)	0.5	0.05	89.60 ± 4.09	4.56
	1.0	0.1	94.41 ± 5.80	6.14
	5.0	0.5	97.53 ± 4.31	4.42
Soil (20)	1.0	0.05	90.20 ± 6.67	7.39
	2.0	0.1	95.58 ± 8.29	8.67
	10.0	0.5	92.72 ± 7.14	7.43

[a] The average recovery comes from three repetition

A micro-column (5 × 1.5 cm i.d. with 5 mL reservoir) was packed with a plug of glass wool and 0.5 cm layer of anhydrous sodium sulfate at the bottom. One gram mixture of florisil and activated carbon (0.97 + 0.03 g) and another 0.5 cm layer of anhydrous sodium sulfate was placed to the above of the sorbent.

The packed column was conditioned with 3 mL petroleum ether/ethyl acetate (80:20) and 3 mL petroleum ether, and then 2.5 mL extracts were added to the column. Elute the column with 12 mL petroleum ether/ethyl acetate (80:20). The eluant was collected in a 50 mL evaporating flask and evaporated to dryness using the rotary vacuum evaporator. The residue was dissolved in 1.0 mL of *n*-hexane, and transferred to a GC sample vial for the instrumental analysis.

Results and Discussion

A study was carried out in order to evaluate the fortified recovery, precision and limit of detection of the analytical method. Carfentrazone-ethyl was fortified to untreated wheat and soil samples at three concentration levels. The fortified samples were analyzed with the above-described procedure with three repetition. The results were shown in Table 1. The recoveries of carfentrazone-ethyl in soil and wheat grains were between 89.60 and 97.53%. The limits of detection (LOD) of carfentrazone-ethyl in wheat and soil samples were 0.002 and 0.001 mg/kg, respectively at a signal-to-noise ratio of 3. The precision of the method regarding as relative standard deviations (RSD) ranged from 4.42 to 8.67%. The recovery and precision results were acceptable according to Residues Analysis Quality Control Guide (General Administration of Quarantine of the People's Republic of China 2002).

The results of dissipation data in soil from Beijing and Jilin were shown in Table 2. As the treatment dosage in

Table 2 Dissipation of carfentrazone-ethyl in soil from Beijing and Jilin, China

Beijing			Jilin		
Time after treatment (h)	Average residue (mg/kg)	Dissipation rate (%)	Time after treatment (h)	Average residue (mg/kg)	Dissipation rate (%)
1	0.0381	–	1	2.08	–
3	0.0235	39.12	2	1.16	44.23
6	0.0182	52.85	4	0.913	56.11
12	0.0128	66.84	6	0.486	76.63
22	0.0064	84.20	9	0.359	82.74
46	0.0043	88.71	24	0.219	89.47
72	0.0033	91.34	48	0.150	92.78
–	–	–	72	0.096	95.38

[a] The treatment dosage in Beijing and Jilin were different, they were 120 and 600 g/hm^2, respectively

Table 3 Terminal residue of carfentrazone-ethyl in wheat grains and soil

Area	Dosage (g/hm^2)	Average residue (mg/kg)	
		Soil	Wheat
Beijing	120	0.0039	ND
	60	0.0031	ND
Jilin	120	0.0046	ND
	60	0.0036	ND

ND not detected, below the LOD of the method

Beijing and Jilin were different (120 and 600 g/hm^2, respectively), the initial concentrations (the concentrations of carfentrazone-ethyl 1 h after treatment) were significantly different from each other (0.0381 and 2.08 mg/kg, respectively). Even though the initial concentration levels were different, the dissipation rate were almost the same. A sharp decline of carfentrazone-ethyl within 10 h after treatment could be observed from the residue data. The amount of carfentrazone-ethyl residue was below 90% of the initial amount 3 days after treatment. The dissipation dynamics of carfentrazone-ethyl in Beijing and Jilin could be described by the following first-order rate equation: $C = 0.0315e^{-0.0705t}$ and $C = 1.3064e^{-0.1001t}$, respectively. As the results showed, carfentrazone-ethyl dissipated rapidly in the soil after application. The half-lives of carfentrazone-ethyl in soil from the two areas were 5.8 and 3.8 h, respectively.

The terminal residue data was shown in Table 3. After the application of the Affinity 40DF at doses of 60 g/hm^2 (recommended dosage) and 120 g/hm^2, respectively, the concentration levels of carfentrazone-ethyl in wheat grains and soil at harvest time were detected. As shown in Table 3, the terminal residues of carfentrazone-ethyl in wheat grains were below the limit of detection, and the residues of carfentrazone-ethyl in soil from Beijing and Jilin were also very low (around 0.003–0.005 mg/kg). The maximum residue limits (MRL) established by US EPA for the carfentrazone-ethyl in wheat grain is 0.1 mg/kg. Obviously it would be acceptable to spray the Affinity 40DF under the recommended dosage due to its low residue in the soil and plants and short half-life. Therefore, carfentrazone-ethyl could be considered as a good alternative for the high resistance herbicide in China, and used in the wheat field safely.

Acknowledgments This study was sponsored by FMC Corporation.

References

Dayan FE, Duke SO, Weete JD, Hancock HG (1997) Selectivity and mode of action of carfentrazone-ethyl, a novel phenyl triazolinone herbicide. Pestic Sci 51:65–73

General Administration of Quarantine of the People's Republic of China (2002) Residues Analysis Quality Control Guide, Beijing, People's Republic of China

Liu L, Gao SB, Lin FG (2000) The using technology of Affinity 40DF. Chin J Pestic 39(8):41–42

Thompson WM, Nissen SJ (2000) Absorption and fate of carfentrazone-ethyl in *Zea mays*, *Glycine max*, and *Abutilon theophrasti*. Weed Sci 48: 15–19

United States Environmental Protection Agency, office of prevention, pesticides and toxic substances (7501C), Pesticide fact sheet 128712 (1998) http://www.epa.gov/opprd001/factsheets/carfentrazone.pdf