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Environmental Behavior of Profenofos Under Paddy Field Conditions

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Abstract The environmental behavior of 40% profenofos EC under paddy field conditions was studied. After application of 40% profenofos EC at 900 g a.i./ha level, the initial deposits of profenofos on rice plant, soil and water were found to be 32.700, 0.224 and 3.854 mg/kg respectively. Half-lives ($t_{1/2}$) of profenofos on those substrates were observed to be 5.47, 3.75 and 3.42 days respectively. The residue levels of profenofos on rice straw, soil and rice grain were significantly affected by the dosage and frequency applied. The obtained results might help to recommend the suitable dose and calculate the safety period of profenofos application.

Keywords Profenofos · Dissipation · Residues · Rice · Soil · Water

Rice (*Oryza sativa* L.) is a staple food for nearly one-half of the world's population, which is often attacked by a number of insects during its growing period. It is estimated that the rice yield losses caused by insects ranging from 31.5% in Asia to 2% in Europe (Heinrichs 2009). Spraying insecticides is one of effective insects control technologies, and has applied in agriculture for a long time. However, pests will develop a resistance to a chemical through selection, after they are exposed to a pesticide for a prolonged period it no longer kills them as effectively. Pesticide rotation is one of effective tactics to avoid resistance caused by such situation. So pesticides with satisfactory control effect in one field are often attractive in another field. Profenofos ((*RS*)-*O*-4-bromo-2-chlorophenyl *O*-ethyl *S*-propyl phosphorothioate) is a wide-spectrum insecticide with easy biodegradation and has been used to control pests in cotton, fruit trees, and vegetables and so on. Hence insecticide factory want to produce new formulation of profenofos for pest control in paddy field. However, no report about the environmental behavior of pesticide in open field is available for building guidance to its application. The present investigation was therefore undertaken to study the dissipation and residues of profenofos in/on rice, soil and water under paddy field conditions.

Materials and Methods

The field experiment was laid out in Jiangsu province of China (118.78° E, 32.04° N) during summer season 2009 in a plot size of 30 m^2 with three replications per treatment. Insecticide profenofos 40% EC was sprayed, and two dosages (600 and 900 g a.i./ha) were tested. In dissipation experiments, high dosage was applied, then rice plant (about 1 kg), soil (0–10 cm, about 200 g) and water (about 200 mL) were sampled randomly from each plot at 0 (2 h), 1, 3, 7, 10, 14, 21, 30, 45 and 60 days after application. For easy controlling, experiments of dissipation in soil and water were carried out in black plots (without crops, depth

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of water keep in 5 cm). In residues experiments, both high and low dosage with two or three applications (7 days interval each) were applied, and the last spray was applied 7, 14 or 21 days before harvest. Then rice straw (about 1 kg), rice grains (about 2 kg) and soil (0–15 cm, about 1 kg) were sampled randomly in harvest time. Rice grains were divided into brown rice and rice hull by a miniature rice sheller for profenofos detection. For control treatment, no pesticide was sprayed and samples were collected as experimental treatment. All samples were stored in deep freeze (−20°C) until detection.

The representative powdered rice straw sample (5 g) from the stored replication was extracted with 40 mL acetone-*n*-hexane (1:1, v/v) mixture for 30 s by homogenate with ULTRA TURRAX, then 0.3 g activated charcoal powder were added to decolorize for 30 min on a mechanical shaker. The contents were then filtered and 10 mL filtrate was evaporated to dryness by nitrogen blowing at 40°C and residues were dissolved in 1 mL chromatographic pure methanol and filtered (0.22 μm) for LC-MS/MS analysis. Soil samples (20 g) were also extracted with 40 mL acetone-*n*-hexane (1:1, v/v) mixture, but for 5 h on a mechanical shaker, then filtered, evaporated and dissolved as rice straw samples. Water samples (5 mL) were extracted thrice by dichloromethane (5 + 3 + 2 mL), and then extractants were collected and evaporated, dissolved as before. Ten grams of powdered brown rice or rice hull were extracted with 40 mL acetone-*n*-hexane (1:1, v/v) mixture for 1 h on mechanical shaker, the contents were then filtered and 10 mL filtrate was evaporated to dryness as before. The residues were dissolved in 1 mL chromatographic pure methanol, and 50 mg C18-bonded silica dispersant sorbent (SUPELCO, US) were then added. After vortex for 30 s, the contents were filtered (0.22 μm) for LC-MS/MS detection.

The contents of profenofos were determined by liquid chromatography coupled to tandem quadrupolar mass spectrometry (LC-QQQ) (Agilent G6410A QQQ, US) under multiple-reaction monitoring mode (MRM). Matrix-matched calibration standards with a series of concentration were used to developing calibration curve. The concentrations of profenofos in different samples were calculated with the help of their respective matrix calibration curve. The limit of quantification (LOQ) of profenofos was calculated as previous reference (Sondhia 2008) and found to be 0.005 mg/kg in rice plant (rice straw) and 0.002 mg/kg in the other substrates.

Rice plant (rice straw), soil, water, brown rice and rice hull samples (CK) were spiked with profenofos at different levels and analyzed as per the methodology described above. Percent recoveries of profenofos in those samples were found to be consistent and more than 80% (Table 1).

Table 1 Recoveries of profenofos in different substrates

Substrate	Spiked level (mg/kg)	Recovery % (Mean ± SD, n = 3)
Rice plant (rice straw)	0.10	94.37 ± 8.19
	0.50	95.78 ± 6.07
	1.00	88.86 ± 1.01
Soil	0.01	87.47 ± 8.44
	0.10	81.79 ± 3.55
	0.50	85.06 ± 4.70
Water	0.10	82.90 ± 2.89
	0.50	87.80 ± 1.00
	1.00	91.67 ± 5.04
Brown rice	0.01	99.38 ± 1.84
	0.05	95.12 ± 1.00
	0.10	94.53 ± 3.71
Rice hull	0.01	84.88 ± 6.79
	0.05	82.58 ± 7.28
	0.10	90.68 ± 3.16

Results and Discussion

The results of dissipation of profenofos in rice plant, soil and water were presented in Table 2. After application of 40% profenofos EC at 900 g a.i./ha, the initial deposits of profenofos on rice plant, soil and water, were found to be 32.700, 0.224 and 3.854 mg/kg respectively. The dissipation behaviors of profenofos in all substrates were fitted to first-order kinetic equation ($C = C_0 e^{-\lambda t}$) and the determination coefficient (R^2) of kinetic equation were 0.9222, 0.9694 and 0.9194 respectively. According to kinetic equations, the half-lives ($t_{1/2}$) of profenofos, after application of 40% profenofos EC at 900 g a.i./ha, in different substrates were calculated to be 5.47, 3.75 and 3.42 days respectively.

A combination of both degradation and dissipative mechanisms control overall persistence of a chemical in the natural environments and there aspects are influenced both by the physico-chemical characteristics of the chemical compound and of the environmental matrix (Chandra et al. 2009). It is the difference of environmental features causes the variance of half-life time of profenofos between the present investigation and other reports (Pramanik et al. 2005; Romeh et al. 2009; Renuka et al. 2006).

Residues of profenofos in rice straw, soil, brown rice and rice hull after applying different dosage and frequency of 40% profenofos EC were presented in Table 3. It showed that the residues of profenofos were significantly affected by the dosage and frequency applied. It is reasonable that, the residues of profenofos are increased as the application level and frequency increase. After application of profenofos on paddy field, it persisted mainly on rice

Table 2 Dissipation of profenofos in rice plant, soil and water after applying 40% profenofos EC at 900 g a.i./ha level

Days after application	Content of profenofos (mg/kg) (Mean ± SD, n = 3)		
	Rice plant	Soil	Water
0(2 h)	32.700 ± 6.283	0.224 ± 0.015	3.854 ± 0.133
1	11.993 ± 5.043	0.212 ± 0.008	3.585 ± 0.373
3	8.026 ± 3.257	0.167 ± 0.023	3.164 ± 0.489
7	4.050 ± 0.685	0.064 ± 0.001	0.730 ± 0.024
10	3.722 ± 0.421	0.054 ± 0.009	0.667 ± 0.022
14	1.387 ± 0.417	0.016 ± 0.001	0.317 ± 0.044
21	0.638 ± 0.192	ND	ND
30	0.138 ± 0.054	ND	ND
45	0.096 ± 0.050	ND	ND
60	ND[a]	ND	ND
Kinetic equation	$y = 12.784e^{-0.1268x}$	$y = 0.2559e^{-0.1846x}$	$y = 4.322e^{-0.2029x}$
$T_{1/2}$(days)	5.47	3.75	3.42

[a] Non-detectable

Table 3 Residues of profenofos in rice straw, soil, brown rice and rice hull after applying different dosage and frequency of 40% profenofos EC

Dosage and frequency	Interval period[a] (day)	Content of profenofos (mg/kg) (Mean ± SD, n = 3)			
		Rice straw	Soil	Brown rice	Rice hull
600 g a.i./ha	7	1.047 ± 0.405	0.031 ± 0.003	0.048 ± 0.008	0.942 ± 0.019
2 applications	14	0.882 ± 0.028	ND[b]	0.028 ± 0.004	0.754 ± 0.030
	21	0.480 ± 0.092	ND	0.016 ± 0.005	0.422 ± 0.018
600 g a.i./ha	7	1.943 ± 0.060	0.036 ± 0.002	0.103 ± 0.018	1.599 ± 0.016
3 applications	14	1.020 ± 0.070	0.022 ± 0.001	0.053 ± 0.006	1.357 ± 0.147
	21	0.350 ± 0.063	ND	0.041 ± 0.003	0.441 ± 0.040
900 g a.i./ha	7	1.924 ± 0.434	0.033 ± 0.001	0.237 ± 0.005	2.187 ± 0.091
2 applications	14	0.900 ± 0.024	ND	0.080 ± 0.008	1.058 ± 0.047
	21	0.677 ± 0.054	ND	0.052 ± 0.002	0.655 ± 0.051
900 g a.i./ha	7	5.809 ± 0.862	0.058 ± 0.018	0.341 ± 0.034	3.978 ± 0.291
3 applications	14	1.691 ± 0.144	0.025 ± 0.006	0.175 ± 0.007	1.859 ± 0.042
	21	0.807 ± 0.105	0.011 ± 0.001	0.067 ± 0.007	0.873 ± 0.014

[a] Interval between the last application time and rice harvest time

[b] Non-detectable

straw and rice hull. Fresh or processed rice straw and rice hull are used as feeds for ruminants in many regions of China; however, the persistence of pesticide residues is a potential risk. Maximum residue limit (MRL) of profenofos on rice straw and rice hull has not set yet, but it set as 1 mg/kg on cotton seed meal and hulls by Australian government. According to this MRL, 21 days interval was needed to insure the rice straw and rice hull use as feeds safely. Pesticide residues in soil raise a number of environmental concerns, such as adverse impact on succeeding crop and migration to ground water. However, with 21 days interval, the residues of profenofos in soil were undetectable under all application level and frequency, except 3 applications of 900 g a.i./ha. The shelled rice grain is the edible part of rice (*Oryza sativa* L.), and the MRL of profenofos on rice grain recommended by European Union (EU) are 0.05 mg/kg. As indicated in Table 3, the residues of profenofos in brown rice were higher than 0.05 mg/kg after applying at 900 g a.i./ha dosage under all application frequency and interval period. At 600 g a.i./ha dosage, if applied two times the residues were lower than 0.05 mg/kg in all interval period, while three times were applied, 21 days interval was needed to insure it was lower than 0.05 mg/kg.

The residue of pesticide in farm produce was decided by not only field conditions but also conditions after harvest.

As per the local practice, rice grains are dried in the sun and stored in the granary till rice processing. During rice processing, rice grains are hulled and bran layers are removed from the brown rice. The behavior of profenofos in post-harvest period is our further research interest.

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