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Dissipation and residue of 2,4-D isooctyl ester in wheat and soil

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Abstract A simple analytical method was developed to determine the 2,4-D isooctyl ester residue in wheat and soil by gas chromatography coupled with electron capture detector. Using the method, the dissipation and residue of 2,4-D isooctyl ester in wheat field was investigated. The average recoveries of 2,4-D isooctyl ester ranged from 80.1% to 110.0% with relative standard deviations of 2.4% to 16.1%. The pesticide showed a rapid dissipation rate either in wheat seedling or soil, with the half-lives of 1.0 to 3.0 days. The terminal residue results in wheat grain were much lower than the codex MRL (2.0 mg/kg). It could be considered safe to food and environment when using this herbicide for controlling weeds in wheat field.

Keywords 2,4-D isooctyl ester · Dissipation · Residue · Wheat · Soil

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Introduction

Phenoxy acid herbicides are one class of the most commonly used herbicides in wheat to control weeds, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (Liu et al. 2007). Phenoxy acid herbicides are commonly used with some types such as esters, acids, and salts, of which esters have the strongest herbicidal activity. 2,4-D butyl ester is the representative one among all of the 2,4-D compounds (Wang and Ye 2005). However, the phytotoxicity caused by 2,4-D butyl ester could affect the production of agriculture. Therefore, a substitute 2,4-D isooctyl ester (Fig. 1) was selected to control weeds for its higher boiling point, low volatile and drifting property (Li 2008).

There are several methods reported to analyze phenoxy acid. For the thermally instability and low volatility of 2,4-D, derivation was essential in most of the GC analytical methods (Wittmann et al. 1996). The immunoassay (Richman et al. 1996 and Amarante et al. 2003) and isotope dilution method (Beeson et al. 1999) were also introduced. However, these methods were not preferentially chosen for their labor-intensive, time-consuming derivative process and the high cost of immunoassay and isotope dilution. Compared with the analysis method for the acid or salt of phenoxy acid herbicides, the analysis of its ester was different and simple. Ma et al. (2009) developed a gas chromatography coupled with

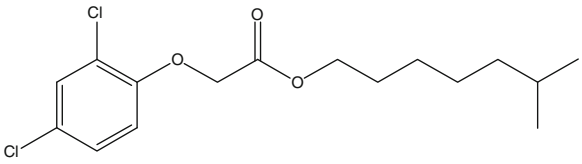

Fig. 1 The chemical structure of 2,4-D isooctyl ester

electron capture detector (GC-ECD) method to analyze 2,4-D isooctyl ester in water extracted by dichloromethane.

There were some similar studies on dissipation of 2,4-D. Fu et al. (2009) found that 2,4-D (2,4-D dimethylamine salt and 2,4-D ethylhexyl ester) can be speedily degraded in natural agriculture soil of Fuzhou, China. He et al. (2010) reported that 2,4-D-dimethylammonium dissipated rapidly either in the wheat or soil. However, to our knowledge, there is no research on herbicide 2,4-D isooctyl ester in wheat field and soil.

In this paper, a GC-ECD method was developed to investigate the dissipation and residue of 2,4-D isooctyl ester in wheat and soil. The field trials were conducted in Anhui (33.38° north, 116.93° east), Hebei (40.82° north, 114.87° east), and Shandong (36.65° north, 117° east) of China. The study aimed to demonstrate the safety following use of 2,4-D isooctyl ester under the recommended dosage and support pesticide registration in China.

Materials and methods

Materials

2,4-D isooctyl ester standard was supplied from National Research Center for Certified Reference Materials, Beijing, China; hexane for chromatography was purchased from Dikma Co., America; a shaker (HZQ-C) was from Harbin Donglian Electron Technology Exploiter Co., Ltd., Heilongjiang Province, China; a centrifuge with 50-mL polyethylene centrifuge tubes was from Conlin Co., Ltd, Shanghai, China; an analytical balance (to 0.001 g; HANGPING JA2003) was from Shanghai, China; a vacuum rotary evaporator (SHB-III) was from Zhengzhou, China; a large-capacity and high-speed desktop centrifuge (RJ-TDL-40B) was purchased from Wuxi, China; and a grinder (IKA A11) was from Beijing, China.

Field trial design

The field trials were conducted in Anhui, Hebei, and Shandong, designed according to "Guideline on pesticide residue trials (NY/T 788-2004)" issued by the Ministry of Agriculture, People's Republic of China. Each site included six experiment plots, which were terminal residue with high and low application dosage (each with three replicated treatments), dissipation in wheat seedling and soil (each with three replicated treatments), and blank control of wheat and soil. Each treatment with an area of 30 m^2 and 1 m distance was used as a buffer zone between the treatments.

The dissipation of 2,4-D isooctyl ester

To investigate the dissipation of 2,4-D isooctyl ester in wheat seedling and soil, 2,4-D isooctyl ester 50% emulsifiable concentrate was applied in wheat field at the dosage of 1,350 g active ingredient (a.i.) ha^{-1}. Both the wheat seedling and soil samples were collected at 2 h, 12 h, 1 day, 3 days, 5 days, 7 days, and 10 days after application. The samples were stored at −20°C before further analysis.

The terminal residue of 2,4-D isooctyl ester

To investigate the terminal residue of 2,4-D isooctyl ester in wheat and soil, both high (1,350 g a.i. ha^{-1}) and low (900 g a.i. ha^{-1}) dosages were applied in two plots separately. The wheat straw, grain, and soil samples were collected at the harvest time. The samples were stored at −20°C before further analysis.

Analytical procedure

For the seedling and straw of wheat, 2.0 g homogenized samples were weighed into a centrifuge tube and 20 mL hexane was added. The samples were shaken in an air bath oscillator for half an hour and then centrifuged at 3,800 rpm for 10 min. Ten milliliter supernatant was taken and evaporated to nearly dryness with the vacuum rotary evaporator under 40°C, then to dryness under a gentle nitrogen stream. The residue was redissolved in 1 mL hexane for GC analysis.

For the wheat grain and soil matrices, 5.0 g samples were weighed into a centrifuge tube and

10 mL hexane was added. The samples were shaken in an air bath oscillator for half an hour and then centrifuged at 3,800 rpm. One milliliter supernatant was transferred into a sample vial for GC analysis.

GC conditions

The 2,4-D isooctyl ester was determined by an Agilent 6,890N gas chromatogram with electron capture detector, attached with an Agilent 7,683 auto-injector and an Agilent Enhanced ChemStation for data acquisition. An HP-5 capillary column (30 m length×0.32 mm i.d. and 0.25 μm film thickness) was used for separation of the compound from the matrix interferences. The injector and detector temperature were operated at 250°C and 280°C, respectively. The sample (1 μL) was injected in splitless mode, and the oven temperature was programmed as follows: 150°C for 2 min, rising to 220°C at a rate of 25°C/min, hold for 4 min, and then rising to 250°C at a rate of 5°C/min, hold for 1 min. The carrier gas was nitrogen with the flow rate of 1 mL/min. The approximate retention time of 2,4-D isooctyl ester was 11.1 min.

Results

Linearity, recovery, and detection limits

To test the linearity, five or six concentrations of matrix-matched standard solutions were prepared. In the wheat seedling, the concentrations were 0.05, 0.10, 0.50, 1.00, and 5.00 mg/L. In the wheat straw, the concentrations were 0.05, 0.10. 0.20, 0.50, and 1.00 mg/L. In the wheat grain, the concentrations were 0.01, 0.025, 0.05, 0.10, 0.25, and 0.50 mg/L. In the soil, the concentrations were 0.01, 0.02, 0.05, 0.10, and 0.50 mg/L. The relative coefficients were ranged from 0.9961 to 0.9986. The limit of detections (LODs) defined as a signal-to-noise ratio(S/N) of 3:1 and ranged from 0.01 to 0.03 mg/kg. The limit of quantifications (LOQs) was determined by the lowest spiking level and ranged from 0.05 to 0.10 mg/kg.

The method accuracy was evaluated by the fortified recovery at three concentration levels with five replicates. The results in seedling, straw and wheat grain, and soil were 83.1–110.0%, 87.7–100.4%, 80.1–93.2%, and 87.1–96.5%, respectively. The relative standard deviations (RSDs) were 2.4–16.1%. The results are shown in Table 1.

Dissipation of 2,4-D isooctyl ester in wheat seedling and soil

The 2,4-D isooctyl ester residue in wheat seedling and soil were detected at different intervals after the application in the field. The results are shown in Figs. 1 and 2. The dissipation kinetics of 2,4-D isooctyl ester could be described by the equation: $C_T=C_0e^{-KT}$ and $T_{1/2}=\ln 2/K$, where T is the time (in days) after pesticide application, C_T is the residue concentration at time T, C_0 is an initial concentration after application (at $T=0$), K is a dissipation coefficient, and $T_{1/2}$ is the half-life of 2,4-D isooctyl ester dissipation.

Figures 2 and 3 show the dissipation of 2,4-D isooctyl ester in wheat seedling and soil. The dynamic equation in wheat seedling of Anhui, Hebei, and Shandong were $y=26.095e^{-0.659x}$, $y=92.385e^{-0.696x}$, and $y=13.653e^{-0.591x}$, respectively. The half-lives were 1.0 to 1.4 days. The dynamic equation in soil of Anhui, Hebei, and Shandong were $y=0.215e^{-0.247x}$, $y=92.385e^{-0.696x}$, and $y=0.235e^{-0.247x}$, respectively. The half-lives were 0.8–2.8 days.

Table 1 The average recoveries, LODs, and LOQs of 2,4-D isooctyl ester in wheat and soil ($n=5$)

Samples	Spiking level (mg/kg)	Average recovery (%)	RSD (%)	LODs (mg/kg)	LOQs (mg/kg)
Seedling	0.10	84.8	3.7	0.03	0.10
	0.50	110.0	6.6		
	1.00	83.1	5.2		
Straw	0.10	87.7	12.8	0.03	0.10
	0.50	100.4	1.9		
	1.00	98.2	16.0		
Grain	0.05	86.2	12.6	0.01	0.05
	0.10	80.1	16.1		
	0.50	93.2	6.0		
Soil	0.05	96.5	13.6	0.01	0.05
	0.1	96.0	15.4		
	0.5	87.1	2.4		

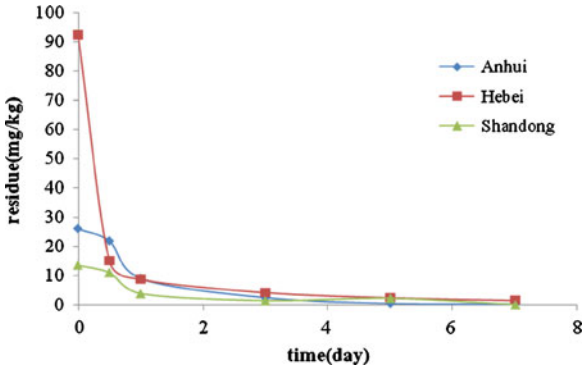

Fig. 2 The dissipation of 2,4-D isooctyl ester residue in wheat seedling of Anhui, Hebei, and Shandong

Terminal residue levels

The terminal residues of 2,4-D isooctyl ester in wheat straw, wheat grain, and soil at harvest time were detected. It was found that the residues of 2,4-D iosoctyl ester in wheat straw sample from three sites were lower than the LOQ value (0.1 mg/kg) except the sample at high-dosage application in Hebei (0.12 mg/kg). The residues in wheat grain from three sites were detected in the range of 0.09 mg/kg to less than the LOD. The residues in soil of the three experiment sites were all below the LOQ value (0.05 mg/kg).

Discussion

In the dissipation experiment of wheat seedling, the initial residue of 2,4-D isooctyl ester in Hebei was much higher than in Anhui and Shandong (92.4 mg/kg in Hebei, 26.1 and 13.7 mg/kg in Anhui and Shandong), the most likely reason might be the plant coverage rate and growth condition of wheat were different in these three experiment plots. The dissipation rate in Hebei was also faster than other two sites. Ninety percent of 2,4-D isooctyl ester were dissipated after 1 day of spraying in Hebei, and it needed 3 days when 90% were dissipated in Anhui and Shandong. According to the experiment records, there was rain in Hebei in the day of spraying, and this made the dissipation rate much faster. The results were in agreement with the previous research. He et al. (2010) showed that 2,4-D-dimethylammonium dissipated rapidly in wheat with a half-life of almost 2.0 days. Cessna and Hunter's (1993) study indicated that the residue of 2,4-D immediately decreased, and after application of 5–6 weeks, the residue of 2,4-D was less than 0.1 mg/kg.

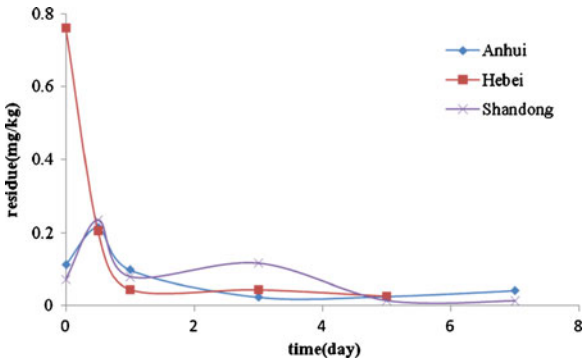

Fig. 3 The dissipation of 2,4-D isooctyl ester residue in soil of Anhui, Hebei, and Shandong

For the precipitation reason in Hebei, the dissipation of 2,4-D isooctyl ester in soil was much faster than in Anhui and Shandong (half-lives of 0.8 day in Hebei and 2.8 days in both Anhui and Shandong). Fu and colleagues' (2009) research showed that the half-life of 2,4-D in natural agriculture soils of Fuzhou was 4.6 days and He et al. (2010) indicated that the half-lives of 2,4-D-dimethylammonium in soil were 2–3 days. Another paper also studied the 2,4-D dissipation in field soils after application of 2,4-D dimethylamine salt and 2,4-D ethylhexyl ester, the results showed that the half-lives were 4–5 days, and either the amine salt or ester forms had the equivalent dissipation rates (Wilson et al. 1997). That is to say, amine and ester forms have little effect on the dissipation of 2,4-D in soil for they are converted rapidly to the same anionic form. Based on these information and this research, it could be concluded that 2,4-D series compound dissipated fast either in wheat seedling or soil. As the amine and ester forms had the same effect on the plant and environment, maybe we should choose the ester form which has stronger activity and higher stability.

In the terminal residue experiment, the maximum residue of 2,4-D isooctyl ester in wheat grain at harvest time was 0.09 mg/kg. The maximum residue limit (MRL) of 2,4-D in wheat grain is set at 0.5 mg/kg by China (GB/T2763 2005) and 2.0 mg/kg by Codex Alimentarius Commission (CAC, http://www.codexalimentarius.net/pestres/data/pesticides/index.html). Those results indicated that it is safe for application of 2,4-D isooctyl ester at

the recommended dosage to control weeds in wheat field.

Conclusion

A simple, sensitive, and accurate residue analytical method was developed using GC-ECD for determination of 2,4-D isooctyl ester in wheat seedling, wheat straw, wheat grain, and soil. The dissipation and terminal residue in wheat and soil were studied to provide a safe and reasonable use of 2,4-D isooctyl ester. It can be seen from the results that the herbicide 2,4-D isooctyl ester showed a rapid dissipation rate either in wheat seedling or soil. The half-lives were about 1.0 day in wheat seedling and almost 2.8 days in soil. The terminal residue results indicated that the residue of 2,4-D isooctyl ester in wheat grain was much lower than the MRL set by China and CAC. It could be considered safe to food and environment to use this herbicide for controlling weeds in wheat field.

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