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Residues and Dissipation of the Herbicide Fenoxaprop-P-ethyl and Its Metabolite in Wheat and Soil

Xiaoxu Chen · Shuang Yu · Lijun Han · Shujun Sun · Yanan Zhi · Wenming Li

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Abstract A method for residue analysis of fenoxaprop-P-ethyl and its metabolite (i.e., fenoxaprop-P) was developed using high performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS). This method was then used to evaluate the residual level and dissipation rate of fenoxaprop-P-ethyl and fenoxaprop-P in the soil and wheat. The half-life of fenoxaprop-P-ethyl in wheat plants and soil was 1.50, 2.36 days in Beijing, and 2.28, 1.79 days in Hubei, respectively. The ultimate residues of the two compounds were undetected in soil, wheat grain and stem at the harvest time, suggesting that fenoxaprop-P-ethyl could be safely used in wheat crops with an appropriate dosage and application.

Keywords Fenoxaprop-P-ethyl · Fenoxaprop-P · Wheat · Soil · Residues · Dissipation

Fenoxaprop-P-ethyl {ethyl-2-[4-[(6-chloro-2-benzoxazolyl) oxy] phenoxy] propanoate} is one of the 2-(4-aryloxyphenoxy) propionic acids (Cocker et al. 1999) which is used for control of annual and perennial grass in barley, wheat, onion and so on. It is an aryloxyphenoxypropionate post-emergence herbicide inhibiting fatty acid synthesis in grasses through inhibition of acetyl CoA carboxylase (Pornprom et al. 2006). Degradation of Fenoxaprop-P-ethyl seems to be mainly hydrolysis to fenoxaprop-P (Lucini and Molinari 2010). The chemical structures of fenoxaprop-P-ethyl and its metabolite fenoxaprop-P were represented in Fig. 1.

Multiple methods for residue analysis of fenoxaprop-P-ethyl in diverse environments have been reported. For example, liquid chromatography with UV detector (e.g., HPLC–UV) was applied to the residue analysis of fenoxaprop-P-ethyl in water (Huang et al. 2007) and rice (Guo et al. 2008). Similarly, gas chromatography with an electron capture detector (ECD) has been used to determine the residue of fenoxaprop-P-ethyl and its metabolite in wheat (Zhu et al. 2000). In addition, the residue analysis of fenoxaprop-P-ethyl and its metabolites has also been reported in diverse media such as soil (Celi et al. 1993), rape (Li et al. 2003) and rice (Lucini and Molinari 2010). The disadvantage of such methods was that they needed lengthy extraction and/or derivation, i.e., labor-expensive and solvent-cost. It is necessary to develop a cost-effective method to determine the residue of fenoxaprop-P-ethyl and its metabolites.

In this study, a simple and rapid method for residue analysis of fenoxaprop-P-ethyl and fenoxaprop-P in wheat and soil was developed. The dissipation dynamics of fenoxaprop-P-ethyl and fenoxaprop-P were investigated in wheat crops and soil under the field conditions. This simple residue analytical method would provide a new tool to evaluate the safe application rate of fenoxaprop-P-ethyl for wheat crops.

Materials and Methods

The fenoxaprop-P-ethyl and its metabolite fenoxaprop-P standards (99% purity) and fenoxaprop-P-ethyl formulations

X. Chen · S. Sun · Y. Zhi · W. Li (✉)
Department of Pesticide, College of Plant Protection,
Henan Agricultural University,
Zhengzhou 450002, People's Republic of China
e-mail: liwenm99@126.com

X. Chen
e-mail: chenxiaoxu666@163.com

S. Yu · L. Han
College of Science, China Agricultural University,
Beijing 100193, People's Republic of China

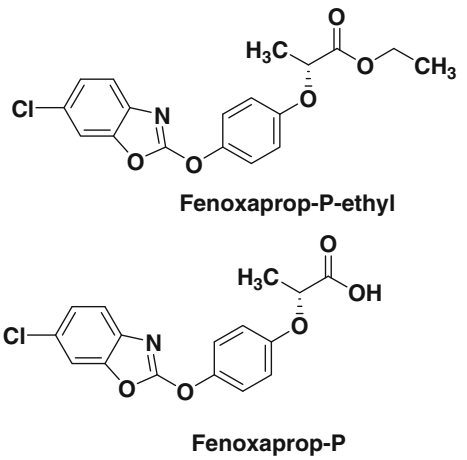

Fig. 1 The chemical structures of fenoxaprop-P-ethyl and fenoxaprop-P

(100 g/L EC) were obtained from Jiangsu Ruihe Chemical Limited Company (Jiangsu, China). High-performance liquid chromatography (HPLC)-grade methanol and acetonitrile was supplied by Fisher Scientific (US). Ultrapure water was purchased from Aquapro Ultrapure Water System (Chongqing, China). Analytical-grade sodium chloride was purchased from Beijing Reagent Company (Beijing, China).

All analyses were conducted with an Agilent 1200 HPLC and an Agilent 6410 B Triple Quad HPLC–MS/MS. The spectral acquisition was done in the positive electron spray ionization for fenoxaprop-P-ethyl and negative for fenoxaprop-P, and multiple reactions monitoring (MRM) was utilized. There were four parent-daughter ion pairs: m/z 362.2/288.1, 362.2/244.2 for fenoxaprop-P-ethyl, and 332.1/260, 332.1/152.1 for fenoxaprop-P. The collision energy was 15, 20, 8 and 15 eV for the four parent-daughter ion pairs, respectively. Nitrogen was used as the dry air. The gas temperature was 350°C and the gas flow rate was 8.0 L min^{-1}, the nebulizer was 35.0 psi, the fragmentors were both 100 V for fenoxaprop-P-ethyl and fenoxaprop-P. A reverse-phase Zorbax C_{18} column (50 mm × 2.1 mm × 1.8 μm particle size) was used as the column and maintained at 30°C. The mobile phase consisted of methanol/water (85/15 by volume), with a flow rate of 0.3 mL min^{-1}. The injection volume was 5 μL. The retention time (R_t) was 1.1 and 0.7 min for fenoxaprop-P-ethyl and fenoxaprop-P, respectively.

Field trials including the dissipation experiments and the final residue experiments were carried out both in Beijing and Hubei, China, in 2009. Spring wheat and winter wheat were used as experimental materials in Beijing and Hubei, respectively. Each experimental field consisted of three replicate plots with an area of 30 m^2 for each plot and was separated by irrigation channels.

When the wheat turned green, fenoxaprop-P-ethyl 100 g/L EC was sprayed on the wheat field. In order to reach the detection limits of the residue analysis method during the grow season, the applied dose was set as 135 g a.i.ha^{-1} for winter wheat and 180 g a.i.ha^{-1} for spring wheat, which was 1.5 times the recommended dosage level. Representative wheat plant and soil samples were randomly collected at about 2 h, 1, 2, 3, 5, 7, 14, 21, 28, and 35 d after spraying. The collected wheat plant samples were comminuted with a grinder. All collected samples were stored in a freezer at −20°C.

The ultimate residue experiment was performed at a low dosage level of 90 g a.i. ha^{-1} for winter wheat and 120 g a.i.ha^{-1} for spring wheat (the recommended dosage), as well as at a high dosage level of 135 g a.i.ha^{-1} for winter wheat and 180 g a.i.ha^{-1} for spring wheat (1.5 times of the recommended dosage), respectively. When the wheat turned green, the high and low dosage treatments were sprayed once. Wheat and soil samples were collected on harvest days after the application of fenoxaprop-P-ethyl (100 g/L EC).

A 10-g subsample of homogeneous soil samples was put into a 50 mL centrifuge tube. Water (5 mL) and acetonitrile (20 mL) were added. The centrifuge tube was placed on a mechanical shaker (HZQ-C, Haerbing Donglian Electron Technology Exploiter Co., Ltd., Heilongjiang Province, China) and shaken for 30 min. After that, sodium chloride (3 g) was added and then vortexed for 1 min on a vortexer (QL-901,Haimen Qilinbeier Instrument Co., Ltd., Jiangsu Province, China). The mixture was centrifuged at 3,800 rpm for 5 min. After the extracts were centrifuged, the supernatant (1 mL) was filtered with a 0.22 μm polypropylene filter to an auto sampler vial for the HPLC–MS/MS analysis.

A subsample of a homogeneous wheat samples (4 gram for wheat plant and grain, 2 gram for wheat stem) was put into a 50 mL centrifuge tube. Acetonitrile (20 mL) was added. The following steps for sample preparation were the same as the steps described above for the soil.

Results and Discussion

The method evaluation was carried out to determine the fortified recoveries, precision and limits of detection of the analytical method. The standard solutions of fenoxaprop-P-ethyl and fenoxaprop-P were added to the untreated soil and wheat plant at levels of 0.01, 0.05 and 0.20 mg/kg and to the wheat grain and stem at levels of 0.05, 0.10 and 0.20 mg/kg. The fortified samples were analyzed using the procedure described with five repetitions. The results suggested that the average recoveries of fenoxaprop-P-ethyl and fenoxaprop-P were 75.36% ~ 112.34% with the

relative standard deviation of 1.61% ~ 11.72%. The limit of detection of the analytical method was 0.005 mg/L at a signal-to-noise ratio of 3, and the limit of quantification was 0.01 mg/kg for soil, 0.02 mg/kg for wheat plant and wheat grain, 0.05 mg/kg for wheat stem. The recovery and precision results were acceptable according to the residues analysis quality control guide (General Administration of Quarantine of the People's Republic of China 2002).

The dissipation trends of fenoxaprop-P-ethyl and fenoxaprop-P in wheat plant in Beijing and Hubei were shown in Figs. 2, 3 and 4. The results showed that fenoxaprop-P-ethyl dissipated rapidly after application. The initial concentration of fenoxaprop-P-ethyl in the wheat plant was 86.7 mg/kg in Beijing and 5.3 mg/kg in Hubei, respectively. The initial residue of fenoxaprop-P-ethyl was much higher in Beijing than in Hubei, which maybe caused by the higher treat dosage on the spring wheat in Beijing, the different wheat varieties and the different planting density in the two sites. The degradation rate was over 99.77% and 85.91% after 14 days of application in Beijing and Hubei, respectively. The half-life of fenoxaprop-P-ethyl in wheat plant in Beijing was 1.50 days and the dynamics could be described by the equation ($C = 82.428e^{-0.4627t}$) with square of coefficient $R^2 = 0.9494$, and the half-life of fenoxaprop-P-ethyl in wheat plant in Hubei was 2.28 days and the dynamics could be described by the equation ($C = 3.0442e^{-0.3045t}$) with $R^2 = 0.6459$. Although the initial residue of fenoxaprop-P-ethyl was higher in Beijing than in Hubei, the half-life was similar in the two sites (1.50 and 2.28 d), which indicated it dissipated rapidly in the wheat plant.

Results in Figs. 5 and 6 showed the dissipation data of fenoxaprop-P-ethyl and fenoxaprop-P in the soil samples in Beijing and Hubei. The concentration of fenoxaprop-P-ethyl in the soil 2 h after application was 0.311 and 0.175 mg/kg in Beijing and Hubei, respectively. The degradation rate was over 90% after 5 days of application both in Beijing and Hubei. The dissipation dynamics of fenoxaprop-P-ethyl in Beijing and Hubei could be described by the following first-order rate equation: $C = 0.2773e^{-0.2941t}$ and $C = 0.1633e^{-0.3882t}$ with the half-life of 2.36 and 1.79 d. The results showed that the dissipation was also fast in the soil, although the concentration level of fenoxaprop-P-ethyl in soil was much lower than in the wheat plant.

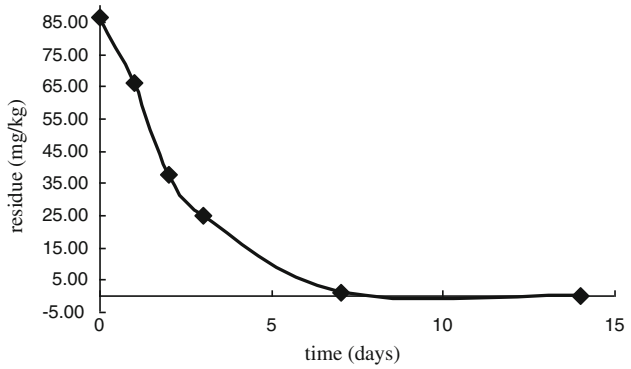

Fig. 2 Dissipation of fenoxaprop-P-ethyl in wheat plant in Beijing, 2009

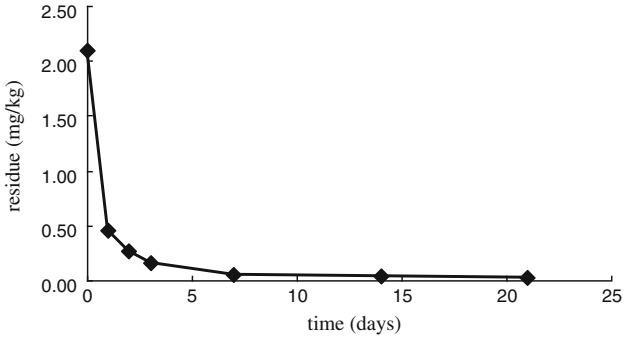

Fig. 3 Dissipation of fenoxaprop-P in wheat plant in Beijing, 2009 Note: For the residue of fenoxaprop-P was much lower than the residue of fenoxaprop-P-ethyl in the wheat plant of Beijing, the figure of the two compounds was separated (Figs. 2, 3)

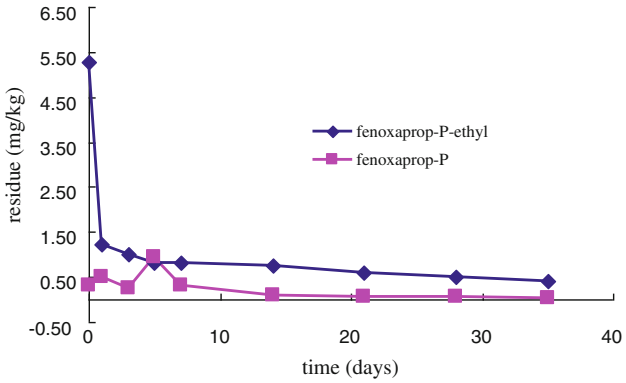

Fig. 4 Dissipation of fenoxaprop-P-ethyl and fenoxaprop-P in wheat plant in Hubei, 2009

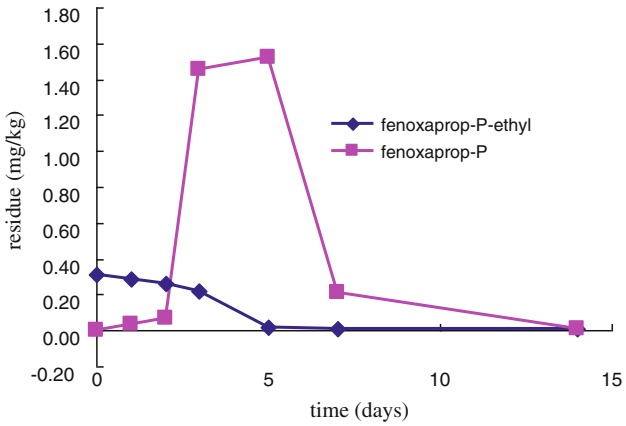

Fig. 5 Dissipation of fenoxaprop-P-ethyl and fenoxaprop-P in soil in Beijing, 2009

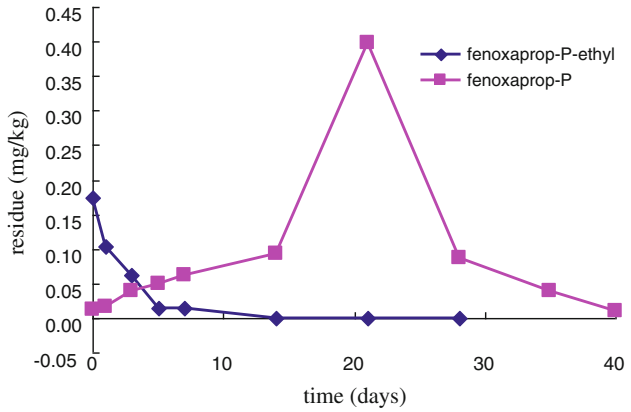

Fig. 6 Dissipation of fenoxaprop-P-ethyl and fenoxaprop-P in soil in Hubei, 2009

With the degradation of the parent compound, the dissipation trend of the metabolite fenoxaprop-P should be increased at the beginning and then declined regularly. However, with the decline of fenoxaprop-P-ethyl, the metabolite fenoxaprop-P in wheat plant was declined regularly in Beijing while the dissipation trend was increased a little firstly and then declined in Hubei. When the residue of fenoxaprop-P-ethyl nearly declined to the lowest, the residue of fenoxaprop-P reached to the highest. In the soil samples, with the decline of fenoxaprop-P-ethyl,the residue of the metabolite fenoxaprop-P was increased firstly in 5 days in Beijing and 20 days in Hubei after application, and then declined regularly on the following days.

In the wheat plant, the highest residue of fenoxaprop-P was much lower than the fenoxaprop-P-ethyl. However, the highest residue of fenoxaprop-P was much higher than the fenoxaprop-P-ethyl in the soil. This phenomenon might indicate that the wheat plant could degrade the fenoxaprop-P, while in the soil, fenoxaprop-P-ethyl could be transferred to fenoxaprop-P and accumulated firstly and then dissipated as normal.

After the application of fenoxaprop-P-ethyl (100 g/L EC) in high dosage and low dosage, the soil and wheat samples were taken during the harvest time from the treated plots. The concentration level of fenoxaprop-P-ethyl and fenoxaprop-P in these samples was determined. The results showed that the concentration of fenoxaprop-P-ethyl and fenoxaprop-P in wheat grain, wheat stem and soil were all below the LOD. The ultimate residues were all undetectable.

America and Australia have established the maximum residue limits (MRL) of fenoxaprop-P-ethyl in wheat as 0.05 mg/kg and 0.01 mg/kg, respectively. In China, the MRL value is 0.1 mg/kg. Our results showed that it is acceptable to spray fenoxaprop-P-ethyl 100 g/L EC at the recommended dosage due to its short half-life time in the wheat plant, and the low final residues which was below the LOD. Fenoxaprop-P-ethyl could be considered as a good alternative to high-toxicity pesticides in China.

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