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Dissipation and Residues of Fluroxypyr-meptyl in Rice and Environment

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Abstract A simple and reliable analytical method for analysis of fluroxypyr-meptyl residue in rice, soil and water was investigated. The residue levels and dissipation rates of fluroxypyr-meptyl (34% AS) were determined by GC–MSD in selected ion monitoring mode. In the supervised field trials, the half-life of fluroxypyr- meptyl in rice plant was in the range 1.25–4.13 days. The half-lives of fluroxypyr-meptyl in soil and water were 2.29 and 1.73 days, respectively. In order to assess the dissipation of fluroxypyr-meptyl in the environment, a laboratory simulated experiment was carried out in soil and water. The terminal residues of fluroxypyr-meptyl in rice plant, husked rice, rice hull and soil samples were undetectable at harvest. It showed that fluroxypyr-meptyl may be safe to use according to the recommended dosage suggested by the corporation.

Keywords Fluroxypyr-meptyl · Dissipation · Residue · Rice

Rice is a widely cultivated crop in China. However, to control pests and diseases in rice, a variety of pesticides are used. Fluroxypyr-meptyl is a synthetical phytohormone and has been applied to many kinds of crops, including wheat, barley, corn, rice and orchard in China. Its structural formula is presented given in Fig. 1. It is rapidly degraded to fluroxypyr in the plant, which is an effective ingredient. Fluroxypyr belongs to the pyridine family and widely used in agriculture. It is usually commercialized as an ester called fluroxypyr-meptyl. Fluroxypyr is effective against a wide range of broadleaf weeds in sugar cane, cereals, sweet corn and olive trees (KJ Kirkland et al. 2001; NN Vettakkorumakankav et al. 2002). Its oral LD_{50} in rats is more than 5000 mg/kg. It is classified by EPA as Toxicity Category II and as ''not likely'' human carcinogen (Aramendía et al. 2005). Toxicity assays demonstrate that it produces nephrotoxicity and impaired renal function in rats (Pastrana-Martínez et al. 2010). Fluroxypyr was analyzed by different analytical methods in various matrices, such as Determination of fluroxypyr Residue in Farm Produce by Capillary Gas Chromatography. Analytical method for fluroxypyr residue in wheat and soil. Determination of fluroxypyr Residue by GC–MS. Residue analysis of fluroxypyr in paddy field water and soil. In recent years, there have been studies on Quantitative Analysis of fluroxypyr-meptyl by Chromatography (Wang et al. 2005).

In the paper, a simple and reliable analytical method was used in sample preparation. The methods to determine fluroxypyr-meptyl residues in rice hull, husked rice, rice plant, water and soil was established and the dissipation dynamics of fluroxypyr-meptyl in rice plant**,** water and soil was investigated as well to study the ultimate residue under good agricultural practices (GAP) use. Up to now, fluroxypyr-meptyl has not been reported in JMPR and there was no paper published to report the residue dissipation of fluroxypyr-meptyl in rice field condition. No residue limit has been established of fluroxypyr-meptyl in rice in China, and the results of this work would be useful in establishing maximum residue level (MRL) or keeping the products safe.

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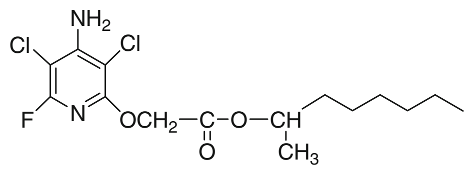

Fig. 1 Tthe chemical formula and exact mass of fluroxypyr-meptyl

Materials and Methods

About 99% fluroxypyr-meptyl standard material was provided by China Agricultural University, China. Ethyl acetate and acetonitrile were of HPLC grade (JT Baker, Xalostoc, Mexico). Sodium chloride, analytical grade, was from Beijing Reagent Company. Anhydrous Magnesium sulfate (Beijing Reagent Company, analytical grade) was heated at 500°C in muffle furnace for 5 h, allowing to be cooling to room temperature before use. Primary secondary amine (PSA) was purchased from Agela Technologies Inc.

The field trials including the dissipation study and terminal residue study. The supervised field trials were carried out in 2009 at three sites: Beijing, Hunan and Jiangsu Province, China. The area of experiment plot was 45 m^2 (10 m × 4.5 m) and each treatment was designed with three replicated plots. A buffer area was maintained between the plots.

The rate of application in dissipation experiments was 956 g (a.i.)/ha(double of the recommended dosage)with one time spray. The rice plant, soil and water were collected in 2 h, 1, 3, 5, 7, 14 and 21 days after spraying of the pesticide. Representative Rice plant, soil and water were stored at −20°C for further analysis. The terminal residue field experiment was applied at two dosage levels, 478 g (a.i.)/ha (low concentration, recommended dosage) and 956 g (a.i.)/ha (high concentration, double of the recommended dosage) with one time spray, respectively. Representative Rice plant, rice sample and soil were collected from each plot at the harvest after spraying, and stored at −20°C for further analysis.

All samples were collected randomly from several points from each plot. Rice plant samples were cut into small pieces using a mechanical slicer. Rice sample was shelled into rice hull and husked rice. Rice hull and husked rice were ground to powder. Soil samples were collected by a depth of 0–15 cm in each plot. Stones and other unwanted materials were removed. Soil samples were dried in the shade at room temperature and screened through 40-mesh sieves. Water samples were collected in the plastic bottles and filtered through a Buchner funnel. All samples were stored at −20°C freezer.

About 10 g rice plant and the husked rice, 5 g of the rice hull samples were weighed into a 50 ml FEP centrifuge tube, 5 ml of distilled water were added, then sample was shaken vigorously for 2 min with vortex mixer. 15 ml acetonitrile, 4 g anhydrous $MgSO_4$ and 1 g anhydrous NaCl were added and samples were vortexed immediately for 1 min. The extracts were then centrifuged for 5 min at 3,800 rpm. An aliquot of 1 ml of the upper layer was placed into a 2.0 ml micro-centrifuge vial containing 50 mg PSA and 150 mg $MgSO_4$. The sample was again vortexed for 1 min and then centrifuged for 5 min at 6,000 rpm with a microcentrifuge. The upper extract was filtered through a 0.45 um pore membrane filter and transferred into a 1.5 ml glass autosampler vial for GC–MS analysis.

About 10 g of homogenized soil sample was weighed into a 50 ml FEP centrifuge tube, 10 ml acetonitrile and 2 ml distilled water were added. The further Sample preparation and cleanup process was similar as the rice samples described above.

About 10 ml of filtered water sample was weighed into a 50 ml FEP centrifuge tube, 5 ml ethyl acetate were added, then the sample was shaken vigorously for 2 min. 3 g NaCl were added and samples were vortexed immediately for 1 min. The extracts were then centrifuged for 5 min at 3,800 rpm. An aliquot of 1 ml of the upper layer was placed into a 2.0 ml micro-centrifuge vial containing 150 mg $MgSO_4$. The sample was again vortexed for 1 min and then centrifuged for 5 min at 6,000 rpm with a microcentrifuge. The upper extract was filtered through a 0.45 μm pore membrane filter and transferred into a 1.5 ml glass autosampler vial for GC–MS analysis.

The fluroxypyr-meptyl was performed by gas chromatograph (Agilent GC 6890) with a 7683B Series split-splitless auto-injector, a 7683 Series Autosampler and a 9575B inter XL EI/CI MSD was used for analysis of pesticides. A Varian Factor Four Capillary Column VF-5 ms analytical column (30 × 0.25 mm i.d. × 0.25 μm film thickness), was used for GC separation. Helium (99.9999%) as carrier gas at a constant flow rate of 1.0 ml/min. An injection volume was 1 μL. Analysis was carried with injection temperature 250°C, and the oven temperature programmed at 180°C for 3 min, raised at 5°C/min to 270°C and finally maintained for 5 min in a splitless mode. The total running time was 26 min. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. MS Source Temperature 230°C, MS Quad Temperature 150°C, Aux-2 Temperature 280°C. Solvent delay was 5.00 min. The analysis was determined by GC–MS-SIM using one quantitation and at least two identification ions. Three ions were chosen: m/z 366, m/z 209 (quantification) and m/z 181. The retention time of fluroxypyr-meptyl was 15.46 min.

Results and Discussion

Linearity was studies in the range 0.02–2.0 mg/L with five calibration points (0.02, 0.05, 0.1, 1.0 and 2.0 mg/L) by matrix-matched standard calibration. Linear calibration graphs were constructed by plotting analyte concentrations against peak areas. Linearity values, calculated as determination coefficients (R^2) were in the range 0.9985–1.0000. (Table 1).

The fortified recovery experiment was studied at three concentration levels (0.02, 0.1 and 1.0 mg/kg). The average recovery of fluroxypyr-meptyl in rice plant, husked rice, rice hull, water and soil ranged from 73.0 to 107.0% with relative standard deviation (RSD) of 2.5%–13.9%. The recovery and RSD was shown in Table 2. The limit of detection (LOD) for fluroxypyr-meptyl was 0.003 mg/kg for water and soil, 0.006 mg/kg for rice hull, husked rice and rice plant samples, at a signal-to-noise (S/N) ratio of 3. The limit of quantification (LOQ) was 0.01 mg/kg for water and soil, 0.02 mg/kg for rice hull, husked rice and rice plant samples, at a signal-to-noise ratio of 10. The

Table 1 Standard curve of fluroxypyr-meptyl in rice plant, husked rice, rice hull, water and soil. (0.02, 0.05, 0.1, 1.0, 2.0 mg/L)

Sample	Regression equation	R^2
Rice plant	y = 62657x-1,186.1	0.9985
Husked rice	y = 33251x + 744.04	0.9994
Rice hull	y = 46628x + 679.89	1.0000
Water	y = 12602x + 83.81	0.9996
Soil	y = 10238x-255.43	0.9994

Table 2 Recovery of fluroxypyr-meptyl in rice plant, husked rice, rice hull, water and soil sample (n = 5)

Sample	Fortified level (mg/kg)	Recovery (%)	RSD (%)
Rice plant	0.02	98.3	10.0
	0.1	100.8	4.7
	1	82.5	2.5
Husked rice	0.02	91.4	6.9
	0.1	84.5	8.7
	1	106.0	2.6
Rice hull	0.02	82.5	12.5
	0.1	73.0	13.9
	1	81.3	3.3
Water	0.02	83.2	7.9
	0.1	91.4	7.0
	1	88.1	4.8
Soil	0.02	98.8	6.0
	0.1	107.0	2.6
	1	84.8	9.3

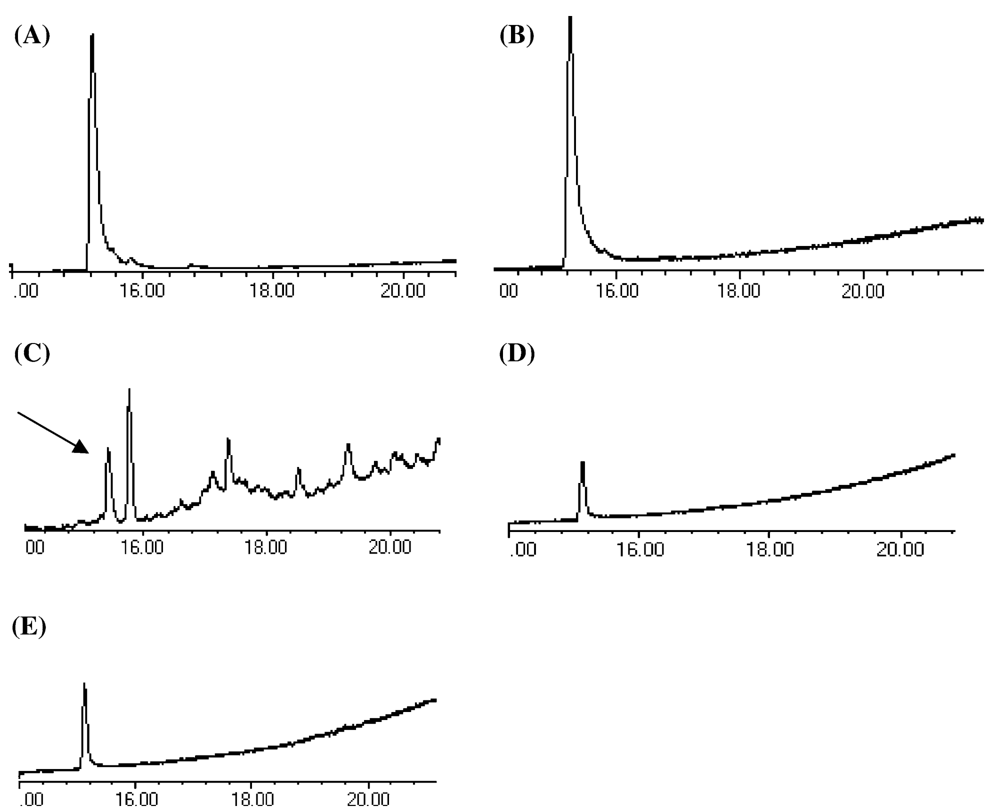

Fig. 2 The GC–MS chromatogram of fluroxypyr-meptyl with matrix samples in SIM mode. **a** in water, **b** in soil, **c** in rice plant, **d** in husked rice, **e** in rice hull

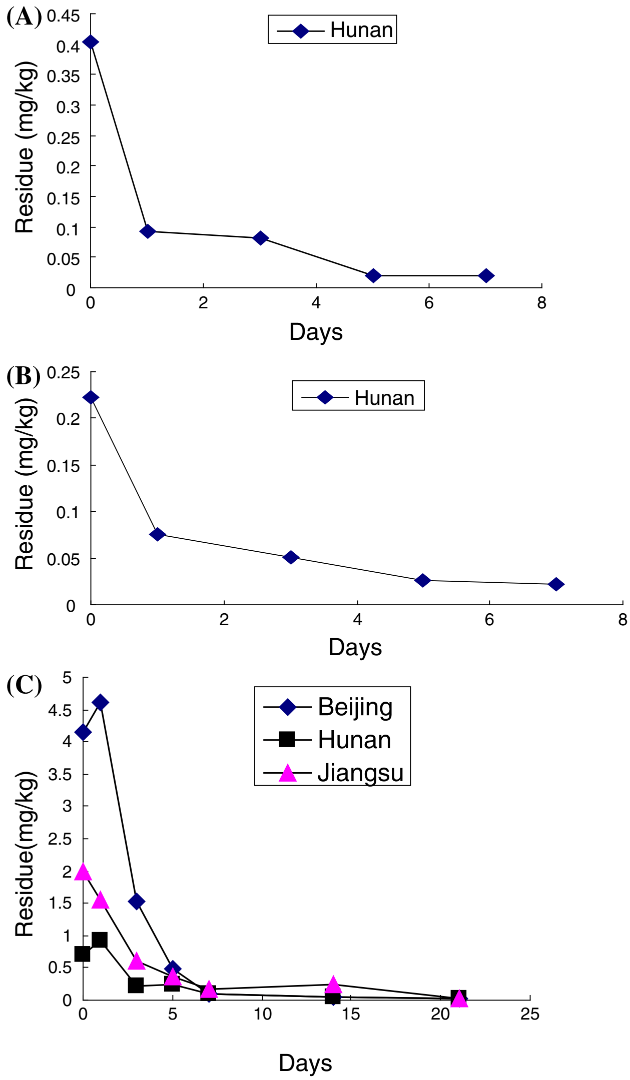

Fig. 3 **a** the dissipation curve of fluroxypyr-meptyl in water samples in three different geographic zones (beijign and jiangsu were <0.02 mg/kg for all water samples). **b** The dissipation curve of fluroxypyr-meptyl in soil samples in three different geographic zones(beijign and jiangsu were <0.02 mg/kg for all soil samples). **c** The dissipation curve of fluroxypyr-meptyl in rice plant samples in three different geographic zones

typical GC–MS chromatograms of fluroxypyr-meptyl are shown in Fig. 2.

The dissipation curve of fluroxypyr-meptyl in rice plant, soil and water samples were listed in Fig. 3. The dissipation process follows the first-order kinetic reaction. The degradation rate constant and half-life were calculated using the first-order rate equation: $C_t = C_o e^{-kt}$, where C_t represents the concentration of the pesticide residue at the time of t, C_o represents the initial concentration after application and k is the dissipation degradation rate constant (days^{-1}). The half-life ($t_{1/2}$) was calculated from the k value for each experiment ($t_{1/2} = \ln 2/k$). $C_t = C_o e^{-kt}$, Half-life and R^2 of residue dissipation were summarized in Table 3. The dissipation rates were more than 90% in rice plant, water and in soil by 21 days after treatment.

The terminal residues of fluroxypyr-meptyl in rice plant, husked rice, rice hull and soil samples were undetectable at harvest after spraying. It is predicted that the application of fluroxypyr-meptyl in rice was low risk for the rice plant and the environment.

The half-life of fluroxypyr-meptyl in rice plants differed among the three experimental sites. Dissipation of fluroxypyr-meptyl in rice plants was faster in Beijing than that in Hunan and Jiangsu because of the effect of environment factors like light, heat, moisture, rainy climate, and growth dilution factor. The dissipation results of fluroxypyr-meptyl in water and soil samples collected from Beijing and Jiangsu were below the LOQ (0.01 mg/kg). In order to assess the dissipation of fluroxypyr-meptyl in the environment, a laboratory simulated experiment was carried out in a pool filled with natural water and soil sample which was collected from rice field of Beijing. According to experimental design, a certain volume of fluroxypyr-meptyl was fortified. The initial concentration in water and soil samples was at 3.09 mg/kg and 0.24 mg/kg, which declined to 0.05 mg/kg and 0.09 mg/kg at 7 days after spraying, respectively. But residue concentration 0.06 mg/kg in soil was detected at 14 days after treatment. The half-life of fluroxypyr-meptyl in water and soil were 1.18 and

Table 3 Half -life and other statistical parameters for fluroxypyr-meptyl dissipation in water, soil and rice plant

Matrix	Locality	Regression equation	Determination coefficient(R^2)	Half-life (day^{-1})
Water	Beijing	-	-	-
	Hunan	$C_t = 0.2382e^{-0.4012t}$	0.8443	1.73
	Jiangsu	-	-	-
Soil	Beijing	-	-	-
	Hunan	$C_t = 0.1438e^{-0.3022t}$	0.8712	2.29
	Jiangsu	-	-	-
Rice plant	Beijing	$C_t = 6.2813e^{-0.553t}$	0.9586	1.25
	Hunan	$C_t = 0.5821e^{-0.1679t}$	0.8945	4.13
	Jiangsu	$C_t = 1.3747e^{-0.1917t}$	0.8743	3.62

6.88 days, respectively. This is the reason why the residue level of all water samples was below LOQ. The dissipation of fluroxypyr-meptyl in natural soil samples was faster in laboratory simulated experiment. Factors influencing the persistence of pesticide in soil are as follows: physical and chemical properties of the soil (texture, especially clay content; organic matter and humus contents, soil moisture, leaching; pH; mineral ion content), climate and the properties of the pesticide (Arias-Estévez et al. 2008, 2006, 2005; López-Pérez et al. 2006; Pateiro-Moure et al. 2008; Yen et al. 2003).

The maximum residue limits established by EU for fluroxypyr-meptyl in rice are 0.05 mg/kg. China has not established MRL for fluroxypyr-meptyl. From the experiments in the three experimental sites, the final residues in rice samples were undetectable at harvest after last application. It is recommended that fluroxypyr-meptyl (34% AS) can be applied in rice at a dosage of 318.8–478.1 g a.i./ha, with spraying 1 time, which is very low risk to the environment and the crops based on its dosage.

A analytical method using GC–MS for the detection and monitoring of fluroxypyr-meptyl in rice plant, husked rice, rice hull, water and soil was established. Average recoveries of fluroxypyr-meptyl in rice plant, husked rice, rice hull, water and soil were in the range of 73.0–107.0%. The relative standard deviation (RSD) ranged from 2.5% to 13.9%. The terminal residues of fluroxypyr-meptyl in rice plant, husked rice, rice hull and soil samples were undetectable at harvest after spraying. Therefore, it could be considered as a low toxicity pesticides for the environment and human beings.

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