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Residual Fate of Herbicide Flumioxazin 50 Sc in/on Wheat

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ABSTRACT

The persistence behaviour of Flumioxazinin wheat were investigated at Chella, Kamarpara, Illambazar, Birbhum, West Bengal, during two consecutive season of 2013-14 and 2014-15. Extraction of the herbicides was performed with acetonitrile followed by dispersive Solid Phase Extraction (d-SPE) clean up with Primary Secondary Amine (PSA: Varian, Harbor City, CA; 40 mm particle size), Florisil (60–100 mesh; Acros, Geel, Belgium) and Graphitized Carbon Black (GCB; United Chemical Technology, Bellefonte, PA: only for plant matrixes). The residue of Flumioxazin were quantified by Liquid Chromatography-mass Spectrometry using multiple reactions monitoring (MRM). The half-life of Flumioxazin was found in the range of 2.59-2.79 days and 3.86-4.93 days for wheat plant and soil respectively. No residue of Flumioxazin was detected in harvest plant sample and soil. It appears from this study that, application of Flumioxazin will not pose any residual toxicity problem when applied in recommended doses.

Key words : *Flumioxazin, Herbicide, Persistence, Soil, Wheat*

Introduction

Wheat is an important crop worldwide and in India, its production increased from a mere 11.0 million tons during 1960-61 to 93.9 million tons during 2011-12 (Chhokar *et al.* 2012). More than eight-fold increase in wheat production was mainly due to the adoption of short stature high yielding varieties, increased fertilizers use, irrigation and herbicides. Weeds are regarded as most disdain to crop production. It has been estimated that crop losses dueto weed competition are greater than those resulting from combined effect of insect pests and diseases (Abbas *et al.*, 2009).

Flumioxazin[7-Fluoro-6-[(3,4,5,6-tetrahydro)-phthalimido]-4-(2-propynyl)-1,4-benzoxazin-3-(2H)-one] is a broad-spectrum contact pre-emergence herbicide. It works by interfering with the plants through production of chlorophyll. It is taken up by plantroot and shoots and translocated in both xylem and phloem (Tomlin, 2006). These will provide a new option for the control of key broadleaf weeds including those with resistance to other herbicides. Some analytical methods regarding the estimation of Flumioxazin are recently reported. A high performance liquid chromatography with UV detection method was developed (Anonymous, 2007) for the quantification of Flumioxazin in soil or sediment and water. Recently, Li *et al.* (2013) developed an analytical method using acetonitrile extraction and

quantification by LC-MS/MS for the determination of Flumioxazin in wheat and soil. There are meager information on the dissipation and dynamics of Flumioxazin on wheat crop in India. Here, authors aimed to establish a method for the quantification of the herbicides using QuEChER approach and to study the degradation of the same in wheat matrix and soil in West Bengal agro-climatic condition. This work would not only help to establish the MRL of Flumioxazin in wheat but also to provide guidance on proper use of Flumioxazin in wheat crop.

Materials and Methods

Field experiment was conducted on wheat (Variety: PBW-343) at ChellaKamarpara G.P.- Chella, Mouza-Chella, P.O.- Daranda, Block- Illambazar, Birbhum, Pin-731236, West Bengal (N 23° 37.374,87° 37.170'E). The formulation Flumioxazin 50 SC was obtained from Sumitomo Chemicals, India. The experiment was designed according to Randomized Block Design (RBD). Each experimental plot was 20 m^2 with 12 rows per plot. The formulation was applied at doses of 70 g a.i. ha^{-1}(T1: recommended dose) and 140 g a.i. ha^{-1} (T2: double the recommended dose) in 500 L water per hectare. Each treatment was replicated thrice has three replication along with an untreated control (T3).

Samples of wheat plant (0.5 kg) and 2 kg of surface soil (0–15 cm depth) were collected randomly from each plot at regular time intervals on 0 (1 h after spraying), 1, 3, 5, 7, 10 and 15 days. Wheat straw (0.5 kg), grain (0.5 kg) and soil (2 kg) samples were also taken at the time of harvest. Samples were brought in the laboratory in plastic bags (< 40 μ) and stored at -22 °C. Wheat includes three matrixes: plant, grain and straw. Each matrix was grounded into small pieces or powder with polytron homogenizer (Model: Polytron, PT-MR-3100 Kinemetica AG, Lucerne, Switzerland). Soil samples were passed through 100 mm sieve. The entire processed sample was kept at -22 °C prior to final analysis.

The analytical standard of Flumioxazin of > 99% purity were obtained from Sumitomo Chemicals, India. All the solvents *viz*. methanol, acetonitrile (HPLC grade) were purchased from J. T. Baker. For cleaning up of the extracted sample, Primary Secondary Amine (PSA: Varian, Harbor City, CA; 40 mm particle size), Florisil (60–100 mesh; Acros, Geel, Belgium) and graphitized carbon black (GCB; United Chemical Technology, Bellefonte, PA: only for plant matrixes) were used. Analytical reagent grade acetic acid was purchased from Merck, India. Magnesium sulphateheptahydrate and soduim chloride was purchased from SRL, India.

The stock solution of Flumioxazin (100 μg/ml) were prepared in methanol and stored in deep freezer. An intermediate standard solution (10 μg/ml) of the herbicides in mixture was prepared by appropriate dilution with the corresponding solvents. The calibration standards (six calibration points) ranging from 0.01 to 0.5 μg/ml were prepared by successive dilutions of the intermediate standard.

The calibration curves for Flumioxazin were obtained by plotting the peakarea against the concentration of the corresponding calibration standards. The limit of detection (LOD) of the test compounds was determined by considering a signal-to-noise ratio of 3 with reference to the background noise obtained for the blank sample. The limits of quantification (LOQ) were determined by considering a signal-to-noise ratio of 10.

The homogenized samples, namely, plant (5g), Soil (10g), straw (2g) and grain (5g) were taken in a 50 ml fluorinated ethylene propylene (FEP) centrifuge tube (Nalgene, Rochester, NY) separately. 10 ml milli-Q water was added and samples were acidified with 0.1 ml acetic acid. It was then vortexed for 1 min. for proper incorporation of the acidified water into sample matrix. After 15 min, 10 ml acetonitrile was added and shaken vigorously for 1 min. Then, 6 g $MgSO_4$ and 1.5 g NaCl was added to it and again vortexed for 2 min followed by 15 minute vertical shaking. Then the sample was centrifuged for 5 min at 5000 rpm. The supernatant (6 ml) was collected to carry out the cleanup procedure.

To carry out the clean-up step, PSA, Florisil and GCB (for plant matrix only) were used. 1.5 ml of the extracted aliquot (plant sample) was taken in a preweighed 2 ml centrifuge tube with 25 mg PSA, 25 mg florisil and 35 mg GCB. For other matrix (straw, soil and grain) 25 mg PSA and 25 mg florisil was taken in 2 ml centrifuge tube for 1.5 ml aliquot. Afterwards, it was centrifuged at 6000 rpm for 5 minutes. It was then filtered through 0.2 μm nylon membrane filter (0.2 μ multipor N66 nylon 6, 6 membrane filter, Pall Corporation) and finally cleaned extract was analyzed by LC-MS/MS.

The recovery experiment was carried out by fortifying fresh untreated plant samples (including

straw and grain) and field soil samples in triplicate with the mixture standard at three concentration levels, *i.e.* LOQ, LOQ × 5 and LOQ × 50. For Flumioxazinthese level were 0.01, 0.05 and 0.50 µg/ml.

Matrix matched standards were employed to evaluate the matrix effect. The blank extracts were prepared in a similar fashion as above with untreated control sample of wheat plant and soil. All six calibration standards were prepared in the blank extracts and analyzed. Quantification of Flumioxazin residue was done by Liquid chromatography coupled with tandem mass spectrometry. The HPLC separation was performed on Alliance 2695 separation module liquid chromatograph (Waters, Milford, MA, USA) equipped with a quaternary solvent delivery system by 20 µl via auto sampler on a reversed phase Symmetry C18 (5 µm; 2.1 × 100 mm) column (Waters, USA) and a Micromass (Manchester, UK) Quattro Micro triple-quadruple spectrometer equipped with an electrospray source (ESI) was used for detection and quantification. Injection volume was 20 µl and the analysis performed with a flow rate of 0.3 ml/min. The mobile phase was composed of (A) water, 5 mM ammonium acetate and 0.1% acetic acid and (B) methanol, 5 mm ammonium acetate and 0.1% acetic acid.

Gradient: 0.0 – 2.0 min – 5.0% B to 95 % B, 2.0-8.0 min – back to the initial condition of 5% B, at 10.0 min, it ends with 5% B.

Estimation of Flumioxazin was performed in positive mode by a single multiple reaction monitoring (MRM) with mass transition from parent ion 354.3 to daughter ion 128.90 for Flumioxazin. A second mass transition was used 354.3 > 81.60 for confirmation. The ratio of the peak area of these two daughter ions for Flumioxazin was 0.149. The corresponding ratio in the positive samples was determined and confirmed in accordance with European Union guidelines (Anonymous, 2002).

Results and Discussion

Quantification of Flumioxazin was done in a single LC-MS/MS method. The linearity of the calibration curve was established in the range 0.01 µg/mlfor Flumioxazin with a correlation coefficient (R2) of the calibration curve > 0.99 (Fig. 1). For matrix calibration, the R2 was found > 0.99. For Flumioxazin, matrix suppression was prominent in plant and soil. For wheat plant matrix, it was 8 – 10 % and 15-18% wheat plant were in the range of 2.59-2.79 days and in soil 3.86-4.93 days. The statistical analysis is

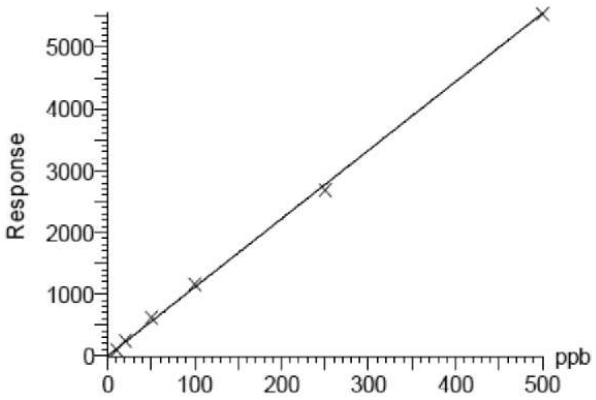

Fig. 1. Calibration Cure of Flumioxazin

in soil.

The concentrations of Flumioxazin in field samples were calculated on the basis of the comparison with the signal in blank samples. For confirmation of residues, the ion ratios pertaining to the two selected mass transitions in actual samples were compared to the ion ratio obtained for calibration standards. Samples showing ion ratios within a range of ± 20% were accepted as confirmatory presence of the said herbicide residues. The average recoveries of Flumioxazin in plant and soil samples at LOQ, LOQ × 5 and LOQ × 50 were 92.35 ± 2.19%, 94.41 ± 3.12%, 96.18 ± 1.38% and 88.39 ± 2.09%, 91.82 ± 3.52% and 90.65 ± 4.80% respectively. The average recovery of wheat straw and grain was 84.23 ± 3.09% and 81 ± 4.65% for Flumioxazin. This complies with the EU DG SANCO criterion (Anonymous, 2000), which requires mean recoveries within the range 70–110%. The initial deposits (2 hr after spraying) of Flumioxazin in soil were found 0.30 µg/g (T1) and 0.66 µg/g(T2) in firstseason and 0.32 µg/g(T1) and 0.65 µg/g(T2) in second season, respectively. In case of wheat plant, initial residual level for Flumioxazin were found 0.74 µg/g(T1) and 1.64 µg/g (T2) in first season and 0.83 µg/g(T1) and 1.74 µg/g(T2) in secondseason respectively. The dissipation of Flumioxazin follows first order kinetics irrespective of any treatment doses and test matrix. More than 50 % of the initial concentration was dissipated within 5 days after application irrespective of any doses and substrate. The half-life (T1/2) of Flumioxazin was calculated using formula given by Hoskins (1961). The half-life of Flumioxazin in

Table 1. Statistical data on the dissipation of Flumioxazin in wheat plant and soil

Substrate	Season	Dose	Regression Equation	R2	Half Life (Days)
Soil	Season-I	T1	Y= -0.075x+2.459	0.989	4.01
		T2	Y= -0.063x+2.782	0.978	4.78
	Season-II	T1	Y= -0.078x+2.494	0.99	3.86
		T2	Y= -0.061x+2.771	0.981	4.93
Plant	Season-I	T1	Y= -0.116x+2.900	0.997	2.59
		T2	Y= -0.110x+3.262	0.991	2.73
	Season-II	T1	Y= -0.112x+2.926	0.999	2.68
		T2	Y= -0.108x+3.263	0.994	2.79

shown in Table 1. No residue was detected in untreated control samples irrespective of treatment dose and season. The residues of Flumioxazin in all substrates during harvest reached below the LOQ value when analyzed at harvest. The degradation of Flumioxazin was found faster in plant than soil. Persistence pattern of Flumioxazin observed in this study is somewhat different as reported by Li *et al.*, 2013. This is probably due to the different climate, soil type, organic carbon (OC) present in soil and chemical and physical properties of the compound (Smith *et al.*, 1977).

The present method established for the detection and quantification of Flumioxazin is cost effective and less time consuming as it comprised of a single method of extraction and single run in LC-MS/MS for both the herbicides. This work would be useful to establish the MRL of Flumioxazin in wheat which will provide guidance on the proper and safe use of this herbicide in India.

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