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Persistence of flumioxazin residues in soybean (*Glycine max*) crop and soil*

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The flumioxazin, 2-[7-fluoro-3, 4-dihydro-3-oxo-4- (2-propynyl)-2H-1, 4- benzoxazin-6-yl] -4, 5, 6, 7-tetrahydro-1H-isoindole-1, 3 (2H)-dione (Bhowmik 2000) is a soil-applied herbicide of the N-phenylphthalimide family and used for weed control in soybean (*Glycine max* L. Merr.) (Han *et al.* 2002, Ferell and Vencill 2003) and potato (*Solanum tuberosum* L.) crop (Wilson *et al.* 2002). Flumioxazin is absorbed by germinating seedlings and stops the first stages of development (Labonne and Capou 1998), weed species then start to bleach and rapidly die off. Flumioxazin is an effective inhibitor of protoporphyrinogen IX oxidase (Protox).

Flumioxazin has a low potential to leach (Hatzios 1998). It degrades rapidly in soil via hydrolysis and microbial degradation and rate of degradation is directly proportional to soil *p*H (Hatzios 1998, Kwon *et al.* 2004), therefore, aqueous hydrolysis in moist soils will be an important process. Despite the wide use of protox inhibitors herbicides in crop, their mode of action remains poorly understood (Theodoridis *et al.* 2000). In addition, most of the information related to their activity has been obtained from studies on diphenyl ether herbicides (Hess 1993, Moreland 1999), whereas little is known about the phthalimides (Labonne and Capou 1998, Tomlin 2000).

Herbicides in the soil, especially those applied pre-planting, pre-emergence and early post-emergence may leave residues on the crop, depending on the chemical, doses and their interaction with the soil properties (Sondhia 2005, 2008). Since herbicides are necessary to achieve maximum yields, their residues may conflict with the crop management. The present paper reports the results of a field experiment aimed to assess the flumioxazin residues applied as pre-plant incorporation or pre-emergence in soybean crop.

Field study was conducted on the farm of National Research Centre for Weed Science, Jabalpur, in rainy (*kharif*) season of 2005 in a randomized block design with 3 replications. The soil characteristics were: clay 35.47%, silt 12.45%, sand 52.09%, nitrogen 300 kg/ha, phosphorus 40 kg/ha, potassium 300 kg/ha, organic carbon 0.80%, electrical conductivity 0.35 mmhos/cm and *p*H 7.3.

'JS 335'soybean was sown on 19 July 2005 and herbicide flumioxazin (50% WP) was sprayed as pre-plant incorporation and pre-emergence, i e 2 days before and after sowing of soybean at 30, 45, 60 and 90 g a i/ha. Three different plots were sprayed for each dose. A further 3 triplicate plots were sprayed with water without any herbicide and maintained as control. The herbicide as per treatment was applied in 500 litre water/ha using flat fan nozzle. The crop was raised under irrigated condition with recommended package of practices.

Soil samples were collected at harvest (106 days), viz 104 pre-plant incorporation and 106 pre-emergence days after spraying of herbicide application. Three kg of 5-soil cores each were randomly taken from each treated and untreated plots avoiding the outer 20 cm fringes of the plots using a soil auger up to a depth of 20 cm from the surface. Pebbles and other unwanted materials were removed manually. The cores were bulked together from each plot, air-dried, powdered and passed through a 3 mm sieve to achieve uniform mixing. Samples from the control plots were collected before the herbicide treated plots for residue analysis.

At harvest 500 g of representative soybean grains and straw samples were collected from flumioxazin treated and un-treated plots. The straw samples were cut in small pieces and air-dried. Soybean grains and straw samples were then grind on mechanical grinder and used for residue analysis. Samples were stored at –20°C, processed and analyzed within 7 days.

Flumioxazin reference analytical standard was obtained from Dr Ehrenstorfer, Germany. All the other chemicals and solvents used in the study were analytical grade obtained from E. Merck, Germany and all the solvents were glass distilled prior to use.

Flumioxazin was extracted as described by Lu *et al.*

*Short note

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(2000), and analyzed by HPLC. 20 g and 50 g each representative soil and crop samples were taken in 250 ml Erlenmeyer flask, and extracted with 50 and 100 ml of methanol: water (4:1) for 1 hr in a horizontal shaker, filtered and content was transferred to a 250 ml separatory funnel and partitioned the solution with methylene chloride 50 ml. Organic layer was collected and dried on anhydrous Na_2SO_4 and passed through activated charcoal. The solvent evaporated to dryness on rotary evaporator, dissolved in 2 ml of methanol and filtered through Pall Nylon 0.45 µm filter paper.

Soybean grains and straw samples were cleaned on a glass column (10 cm × 2 cm i.d.) packed with florisil (1 g) and activated charcoal (0.25 g) between anhydrous sodium sulphate (2 g) at each end. The concentrated extract was added at the top after pre-washing with methanol and eluted with methanol and water (60: 40). Elutes were collected and solvent was evaporated and dissolved in 2 ml methanol.

Flumioxazin residues were analyzed by high-performance liquid chromatography coupled to RF Detector. The excitation and emission wavelengths were set at 280 and 405 nm. The method makes use of Phenomenex C-18 (ODS) column (250 cm × 4.6 mm i.d.) and methanol: water (70:30 v/v) as mobile phase at a flow rate of 0.8 ml/min at ambient temperature. Different known concentration of flumioxazin (25, 2.5, 0.25 and 0.025, 0.001 µg/ml) were prepared in methanol by diluting the stock solution (100 µg/ml). A 20 µl of flumioxazin standards solution was injected and the peak area was measured. Peak area responses at respective concentration were averaged and linearity was observed. Using these condition flumioxazin was eluted at Rt 3.8 minutes. Afterwards 20 µl crop and soil samples were injected to detect flumioxazin residues under the same conditions.

The retention time of flumioxazin was found to be approximately 3.8 min. The limit of detection was 0.001 µg/g and the signal to noise ratio was 3:1. No substrate interferences were observed at this quantification limit as evidenced by control sample analysis. The soil blanks did not exhibit any peak interfering with the retention time of flumioxazin. Therefore, for the soil the extraction did not require any clean up procedure. Response of flumioxazin standards at various concentrations is presented in Table 1. Residues of flumioxazin as detected by HPLC using RF detector in soil, soybean and straw are presented in Table 2. The concentration of flumioxazin residues applied as pre-plant incorporation or post emergence at doses between 30 and 90 g a i/ha were found below the detection limit (<0.001 µg/g) in the soil at harvest, in all the treatments (Table 2).

Table 1 Calibration of flumioxazin standard at different concentration level

Concentration (ppm)	*Average area (mabs)	Standard deviation
25	318.737	+4.802
2.5	68.638	+5.302
0.25	38.934	+2.024
0.025	31.668	+4.659
0.001	9.560	+0.641
R^2	0.99	
Linear equation	Y=11.642 x + 28.835 Intercept 0.851	Slope = –2.409

*Average of 3 replications

Residues in the grains were below the detection limit of 0.001 mg/g in treatment applied as pre-plant incorporation at the doses 30–90 g ai/ha. However, 0.0012, 0.0022 and 0.0031 µg/g residues were detected in treatments where flumioxazin was applied as post emergence at the doses 45, 60 and 90 g a i/ha, respectively. Whereas residues were below the detection limit at 30 g a i/ha (Table 2).

Residues were below the detection limit in the soybean straw in those treatments where flumioxazin was applied as pre-plant incorporation at 30 and 45 g a i/ha, whereas 0.0015 and 0.0024 µg/g were detected at 60 and 90 g a i/ha respectively (Table 2). However 0.0012, 0.0014, 0.0014, 0.0017 µg/g residues were detecting in the treatments where flumioxazin was applied as post emergence at 30–90 g ai/ha.

Low concentration of the pesticide in soil may be compensated by the increased microbial activity due to high microbial activity, thereby increasing the rate of degradation (Johnson and Sims 1993, Sondhia 2005). Besides the organic matter, the clay content can also play an important role in degradation rate of pesticides. In fact, it determines a significantly increase of the microbial biomass. The experimental soil was rich in clay content (35%) that might favoured degradation of flumioxazin in the soil that lead in the low concentration in soil as compare to crop produce at harvest.

Flumioxazin has not been evaluated by the JMPR and there are no codex maximum residue limits for flumioxazin. Though in the present study residues were found below the maximum residue limits set by some European countries and South Africa countries (0.05 and 0.01 mg/kg) but there is still concern for use of flumioxazin because of its persistence in soil and crop produce.

Flumioxazin degrades rapidly in soil water via hydrolysis. The rapid soil dissipation rate indicates flumioxazin is not persistent in soil. Flumioxazin degraded at faster rate in pre-plant incorporation as compared to pre- emergence application (Table 2) as residue were not found in soybean grains in all the doses. On the basis of above findings it can be concluded that flumioxazin application at 30–45 ai g/ha can be safely applied to the soybean crop as pre-plant incorporation and pre- emergence herbicide as the residues were not detected at this application levels neither in soil nor in crop produce, however persistence of flumioxazin residues in crop produce in higher doses (60 and 90 g ai/ha)

Table 2 Harvest time residues of flumioxazin in soybean grains, straw and soil

Matrix	Herbicide residues *(mg/g)							
	Pre-plant incorporation (g ai/ha)				Pre-emergence (g ai/ha)			
	30	45	60	90	30	45	60	90
Grains	BDL	BDL	BDL	BDL	BDL	0.0012	0.0022	0.0031
Straw	BDL	BDL	0.0015	0.0024	0.0012	0.0014	0.0017	0.0017
Soil	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Detection limit (μg/g)	0.001							

*Average of 3 replications; BDL, below detectable limit

at harvest in soybean grain and straw is significant in terms of residual contamination of crop produce as at this concentration metsulfuron-methyl residues were found above the maximum residue limits set by EPA/WHO (0.001 μg/g).

SUMMARY

A field experiment was conducted at National Research Centre for Weed Science, Jabalpur, in *kharif* 2005. Flumioxazin was applied at 30, 45, 60 and 90 g a i/ha rates, as pre-plant incorporation and 2 days after sowing of soybean as pre-emergence herbicide. Soil and crop samples were collected at harvest after herbicide application and analyzed for residues using HPLC. Flumioxazin residues were found below the detection limit in the soil and grains applied as pre-plant incorporation. Residues in the grains and soil were below the detection limit of 0.001 mg/g in treatment applied as pre-plant incorporation at the of doses 30–90 g ai/ha. However 0.0012, 0.0022 and 0.0031 μg/g residues were detected in grains in treatments where flumioxazin was applied as post emergence at the doses 45, 60 and 90 g a.i./ha. Residues were below the detection limit in the straw at 30 and 45 g a.i./ha in, hopre-plant incorporation however 0.0015 and 0.0024 μg/g were detected at 60 and 90 g ai/ha doses respectively. On the basis of above findings it can be concluded that flumioxazin application at 30–45 a i g/ha can be safely applied to the soybean crop as pre-plant incorporation and pre-emergence herbicide.

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