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Determination of imazosulfuron persistence in rice crop and soil

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Abstract Imazosulfuron is a new post-emergence sulfonylurea herbicide. It is highly active at low application rates to control annual and perennial broad-leaf weeds and sedges in rice. There is increasing concerned about the persistence of pesticide residues in soils, crop produce and subsequent contamination of groundwater. Thus persistence of imazosulfuron residues under field condition was evaluated. Imazosulfuron was applied at 30, 40, 50 and 60 a. i. g ha $^{-1}$ rates, 4 days after transplanting of rice as post-emergence herbicide. Soil and plant samples treated with imazosulfuron were collected at 60, 90 and 120 days after herbicide application and analyzed for residues. Rice grains and straw samples were sampled at harvest (120 days). Residues of imazosulfuron in soil were not found after 90 and 120 DAS (days after spraying). Rice grains contained 0.006, 0.009 μg g^{-1} residues at 50 and 60 g ha $^{-1}$ application rates. 0.009 and 0.039 μg g^{-1} residues of imazosulfuron were detected at 50 and 60 g/ha rates respectively in rice straw. Residues of imazosulfuron were not detected applied at 30 and 40 g ha^{-1} in rice grains and straw, respectively and can be safely applied to the transplanted rice.

Keywords Soil · Rice grains · Straw · Imazosulfuron · Hplc analysis

Introduction

At present approximately 20 sulfonylurea herbicides have been successfully marketed in the world due to low application rates, high selectivity and very low mammalian toxicity (Brown and Cotterman 1994; Anderson and Domsch 1993; Tomlin 1997; Roberts 1998). Imazosulfuron, chemically known as 1-(2-chloroimidazo [1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,dimethoxypyrimidin-2-yl) urea (Fig. 1), is a new post-emergence sulfonylurea herbicide. It is highly active at low application levels and used to control most annual and perennial broad-leaf weeds and sedges in paddy and turf (Son and Rutto 2002).

Chemical hydrolysis and microbial breakdown are the most important pathways of sulfonylurea degradation in soil, whereas photolysis and volatilization are relatively minor processes (Molinari et al. 1999). Morrica et al. (2004) reported photolysis of imazosulfuron in aqueous solution under UV light and identified major photodegradation products as (4,6-dimethoxypyrimidine-2-yl)aminocarbonylsulfamic acid, 4,6-dimethoxy-2-ureidopyrimidine and 2,2′-dichloro-[3,3′] bi [imidazo[1,2-a] pyridinyl]. Each of these processes can be influenced differently by the environmental conditions, including soil

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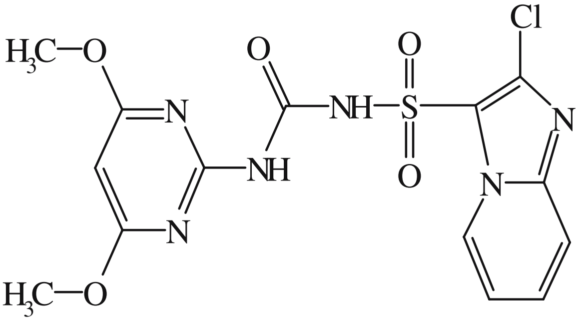

Fig. 1 Structure of imazosulfuron (-(2-chloroimidazo[1,2-*a*] pyridin-3-ylsulfonyl)-3-(4,dimethoxypyrimidin-2-yl)urea

properties. Imazosulfuron degrade rapidly in low pH soil (Morrica et al. 2001a). Mikata et al. (2003) found ^{14}C imazosulfuron in the upper 30 cm soil layer, and no ^{14}C imazosulfuron was detected below a depth of 50 cm and concluded that imazosulfuron and its degradation products in soils translocated into groundwater only slightly. Morrica et al. (2002) evaluated environmental fate of imazosulfuron, in four different Italian soils, varying with respect to their physical and chemical properties and found imazosulfuron degraded slowly in the acidic sandy loam soil due to the high adsorption coefficient which allows protection of imazosulfuron from microbial attack. Hydrolysis of imazosulfuron occurs in acidic conditions (Morrica et al. 2001a). Literature said that imazosulfuron adsorbs poorly on soil and can leach deeper in the soil horizon where anaerobic like conditions may occur (Morrica et al. 2000).

There is increasing concerned about the persistence of pesticide residues in soils, crop produce and subsequent contamination of groundwater. In particular, their mobility, rate of degradation and solubility govern their potential to contaminate waters from different routes. It is essential that contamination by pesticides should be prevented in order to safeguard drinking water supplies and to protect fish and other aquatic life (Environment Agency 1997). Extensive research has been carried out on the persistence and mobility of sulfonylurea herbicides both in laboratory and field studies (Walker et al. 1989; Schneiders et al. 1993; Yutai et al. 1999; Sondhia and Singhai 2006; Sondhia et al. 2007). Sulfonylurea herbicides are weak acids and they exist primarily in the anionic form in agronomic soils. Consequently, sulfonylurea herbicides are generally weakly adsorbed by soil. Also, their adsorption decreases when soil pH increases, as a result of the increased amount of anionic species in solution (Beyer et al. 1988).

In India, rice is the first most important food crop in terms of production. Although there are several reports on the efficacy of imazosulfuron against various weeds in rice (Usui 2001; Akiyama et al. 2002; Son and Rutto 2002), but very few reports on the methods of analysis and its environmental fate in rice agro-ecosystems. Some authors suggested a potential risk of sulfonylurea herbicides (Fletcher et al. 1993; Peterson et al. 1994; Fahl et al. 1995), which are active at very low rate of application. Hence present study was conducted to evaluate the environmental fate of imazosulfuron, in soil and crop produce. The use of four different doses might help to recommend the suitable dose in terms of possible residue contamination by imazosulfuron.

Material and methods

Field dissipation study

A field experiment was conducted at the experimental farm of National Research Centre for Weed Science, Jabalpur, India, in *Kharif* 2005 in a randomized block design with three replications. Fifteen different plots each with a dimension of 5×4 m^2 were prepared. One metre distance was maintained between the plots. All four sides of the plots were protected by soil boundaries (bunds) raised to a level of approximately 30 cm height and 30 cm width. Rice seedlings were collected from the nursery and transplanted as per the local agriculture practice at a spacing of 20 cm and 15 cm between the plants. Four days after transplanting of rice seedlings, four different doses of imazosulfuron (10% SC) viz. 30, 40, 50 and 60 g ha^{-1} were sprayed with Knap-sap sprayer using flat fan nozzle. A further three triplicate plots were sprayed with water without any herbicide and maintained as control.

Collection of samples

Soil samples

Soil samples were collected at 60, 90 and 120 days after application of herbicide. 3 kg of five-soil cores each were randomly taken from each treated and untreated plot 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. The soil was clay loam in texture (clay 35.47%, silt 12.45%, and sand 52.09%), nitrogen 300 kg ha^{-1}, phosphorus 40 kg ha^{-1} and available potassium 300 kg ha^{-1} with organic carbon 0.80%, EC 0.35 mmhos cm^{-1} and pH 7.2.

Rice plants

Two hundred fifty gram plant samples at 60 and 90 days were collected from each treated and untreated plot. The plant samples were cut into small pieces and used for analysis.

Collection of rice grains and straw samples

At harvest 500 g of representative rice grains and straw samples were collected from imazosulfuron treated and untreated plots. The straw samples were cut in small pieces and air-dried. Rice grains and straw samples were then ground on mechanical grinder and used for residue analysis.

Sample storage

Samples were stored at −20°C, processed and analyzed within 7 days.

Analytical methodology

Imazosulfuron reference analytical standard was obtained from ACCU standard, USA. Imazosulfuron commercial grade was obtained from Sumitomo. All other chemicals and solvents used in the study were analytical grade (E Merck, Germany) and all the solvents were glass distilled prior to use.

An analytical method was developed by high-performance liquid chromatography (HPLC). The HPLC system consisted of a Shimadzu instrument equipped with degasser, LC-10 ATVP pump, SPD-M10 AVP diode array detector (DAD) and Rheodyne injection system. The method makes use of Phenomenex C-18 (ODS) column (5 μm particle size, 250×4.6 mm i.d.) and acetonitrile: water (70:30 v/v) as mobile phase at a flow rate of 1 ml min^{-1} at 230 nm. 20 μl of the aliquot of standards and samples was injected by using micro syringe. Using these condition sulfosulfuron was eluted at Rt 3.71 min.

Extraction of imazosulfuron from various matrix

From soil

Soil samples (25 g) were extracted with acetonitrile: dichloromethane: 1.0 M ammonium hydroxide (30: 8: 2) using horizontal shaker for 1 h. The contents were filtered through a Buchner funnel. The extraction was repeated twice (50+25 ml). The filtrates were concentrated on rotary vacuum evaporators to about 2 ml.

Extraction from rice grains and straw

Twenty five grams of powdered rice grains and straw samples collected from imazosulfuron treated and untreated plots were extracted twice with acetonitrile: water (150 ml) on horizontal shaker for 2 h. The contents were filtered, collected and solvent was evaporated to approximate 2 ml in a rotary vacuum evaporator.

Cleanup

The concentrated extracts of soil samples were filtered through Pall Nylon 0.45 μm filter paper prior to HPLC injection.

Rice grains and straw samples were subjected to glass column cleanup. A glass column (10 cm×2 cm i.d.) was packed with celite (1 g) and activated charcoal (0.25 g) between anhydrous sodium sulfate (2 g) at each end. The concentrated extract was added at the top after pre-washing with acetonitrile and eluted with acetonitrile and water (70: 30). Elutes were collected and solvent was evaporated on a rotary vacuum evaporator and dissolved in 2 ml acetonitrile prior to analysis.

Recovery and detection limits

Different known concentration of imazosulfuron (0.0005, 0.005, 0.05, 0.5 and 5 μg ml^{-1}) was prepared in acetonitrile by diluting the stock solution (1,000 μg ml^{-1}). Twenty microliters was injected and the peak area measured. Validation of the method was also performed in terms of recovery studies before analysis of soil, rice grains and straw samples. The recovery study was conduced for different matrix. 10 g of control sample was taken and 1 ml of 0.1 and 0.5 μg ml^{-1} standard solution of imazosulfuron was added uniformly on the surface of the matrix and extracted as described earlier. Recovery studies were conducted for soil, rice grains and straw. At each sampling interval of matrix (soil, rice grains and straw); samples were spiked with known concentration of imazosulfuron and recovery was determined before the analysis of unknown samples.

Results and discussion

Recovery and detection limit

The recovery and detection limit of imazosulfuron are shown in Tables 1 and 2. Residue values were not corrected for recovery. The retention time of imazosulfuron was found to be approximately 3.71 min. The calibration curve was linear from 0.0005 to 5 μg ml^{-1} (Fig. 2). Instrumental detection limit for imazosulfuron was calculated by repetitive four injections and using following equation;

$$IDL\left(\mu g\, ml^{-1}\right) = \frac{S.D. \times St \times C}{A}$$

S.D. – Standard deviation; St – student coefficient; C – Concentration of pesticide (μg ml^{-1}) and A – mean area of the corresponding pesticide at that concentration.

Table 1 Calibration of imazosulfuron by HPLC method

Concentration (μg/ml)	Average area	Standard deviation
5.0	66,536,435	±5,888,929
0.5	6,910,200	±797,305.4
0.05	876,871.1	±81,839.43
0.005	124,577.3	±25,692.58
0.0005	55,356	±63,692.64

*Three injections.

Table 2 Recovery of imazosulfuron from rice grains and straw

Matrix	Amount added (μg g^{-1})	Amount recovered* (μg g^{-1})	Recovery (%)
Rice grains	0.10	0.07	70
	0.50	0.39	78
Rice straw	0.10	0.09	90
	0.50	0.45	90
Soil	0.10	0.09	90
	0.50	0.48	96

*Average of three replications.

Estimated method detection limit (EMDL) for imazosulfuron was calculated from the following formula.

$$EMDL\left(\mu g\, ml^{-1}\right) = \frac{IDL \times V \times 100}{Mx\,\%\,R}$$

IDL=Instrument detection limit; V – final volume of the sample; M – mass of the sample R=% recovery.

The limit of detection was 0.5 μg l^{-1} and the limit of quantification was 0.001 μg g^{-1}. No substrate interferences were observed at this quantification limit as evidenced by control sample analysis. The imazosulfuron recovery varied from 70–90% for rice grains and straw samples fortified with 0.1 and 0.5 μg g^{-1} of imazosulfuron. Recovery was acceptable upto fortification level of 0.1 μg g^{-1}.

The recoveries of imazosulfuron from soils at different concentration levels were satisfactory being within the range 90–96%, confirmed a good repeatability of the method (Table 2). The soil blanks did not exhibit any peak interfering with the retention time of imazosulfuron.

The equations of analytical calibration graphs, obtained by plotting peak areas against concentrations of imazosulfuron within the range of 5 to

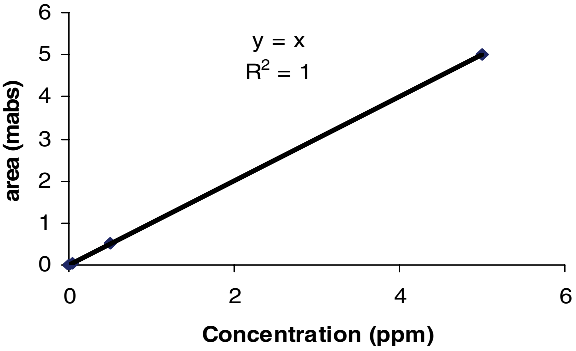

Fig. 2 Calibration curve of imazosulfuron injected at 5 to 0.001 μg ml^{-1} levels

Table 3 Detection of imazosulfuron residues in rice grains and straw at harvest

Dose (g ha^{-1})	Residues* (μg g^{-1})	
	Rice grains	Straw
30	ND**	ND
40	ND	ND
50	0.006±0.004	0.009±0.001
60	0.009±0.001	0.039±0.013

*=average of three replications

**ND=Not detected.

0.0005 μg ml^{-1} was, y=10,000,000x+196,100, and the correlation coefficient was 1.

Residues of imazosulfuron in soil

Residues of imazosulfuron as detected by HPLC in soil are presented in Tables 3 and 4. The concentration of imazosulfuron in the soil at 60 days was 0.002, 0.006, 0.007, 0.010 μg g^{-1}. There was rapid decline in the concentration of imazosulfuron and by the 90 days residues degraded to below detectable level and no residues of imazosulfuron were detected in the soil (Tables 3 and 4).

Residues in the rice plant

In the rice plant 0.009, 0.029, 0.031, 0.064 μg g^{-1} residues were detected at 60 days, which got down to 0.002, 0.013, 0.014, 0.032 μg g^{-1} respectively (Table 4) at 90 days in the 30, 40, 50 and 60 g ha^{-1} of imazosulfuron treated plots which show slow degradation of imazosulfuron residues in rice plants.

Residues in the rice grains and straw

At harvest (120 days) imazosulfuron residues were not detected in rice grains at 30 and 40 g ha^{-1} treated plots. However 0.006 and 0.009 μg g^{-1} imazosulfuron residues were detected in rice grains where imazosulfuron was applied at 50 and 60 g ha^{-1} rates. Imazosulfuron residues in rice straw were not detected at 30 and 40 g ha^{-1} treated plots, however 0.009 and 0.039 μg g^{-1} residues were detected where imazosulfuron was applied at 50 and 60 g ha^{-1} rates, respectively (Table 3).

In the soil the decrease in the concentration of the pesticide in soil is compensated by the increased microbial activity, thereby increasing the rate of degradation (Bolan and Baskaran 1996; Kanazawa et al. 1988; Johnson and Sims 1993; Shelton and Parkin 1991; 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 (Jenkinson and Ladd 1981; Chaussod et al. 1986). The soil was rich in clay content (35%) that might favoured degradation of imazosulfuron in the soil so that by 90 and 120 days imazosulfuron degraded completely and hence no residues were detected (Table 3). Morrica et al. (2001b) also reported rapid dissipation of imazosulfuron in the field condition. In the sulfonylurea herbicides, greater adsorption at lower pH has mainly been attributed to adsorption of the molecular forms (Mersie and Foy 1986; Shea 1986; Wehtje et al. 1987). The pH of the experimental soil was approximately neutral (7.2) which allowed less adsorption of the imazosulfuron to the soil and

Table 4 Detection of imazosulfuron residues in soil and green plants at various time intervals

Dose (g ha^{-1})	Residues* (μg g^{-1})				
	Soil			Plant	
	60***	90	120	60	90
30	0.002±0.001	ND**	ND	0.009±0.007	0.002±0.003
40	0.006±0.001	ND	ND	0.029±0.005	0.013±0.005
50	0.007±0.001	ND	ND	0.031±0.009	0.014±0.005
60	0.010±0.001	ND	ND	0.064±0.024	0.032±0.020

*+ average of three replications

**ND=Not detected.

***=Days after spraying.

hence residues were not detected after 90 and 120 days.

On the basis of above findings it can be concluded that imazosulfuron application at 30 and 40 g ha^{-1} can be safely applied to the transplanted rice crop as post-emergence herbicide as the residues were not detected at this application levels neither in soil nor in crop produce, however persistence of imazosulfuron residues in crop produce in higher doses (50 and 60 g ha^{-1}) at harvest in rice grains and straw is significant in terms of residual contamination.

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