Bull Environ Contam Toxicol (2009) 83:799–802
DOI 10.1007/s00128-009-9822-5

Persistence of Metsulfuron-Methyl in Paddy Field and Detection of Its Residues in Crop Produce

Shobha Sondhia

Received: 5 March 2009 / Accepted: 25 June 2009 / Published online: 16 July 2009

Abstract Among sulfonylurea herbicides, metsulfuron-methyl [methyl 2-(4-methoxy-6-methyl-1,3,5-triazine-2-ylcarbamoylsulfamoyl) benzoic acid] is widely used due to its selectivity against a wide range of weeds in cereal, pasture, and plantation crops. Use of persistent herbicides has increased risk of accumulation of residues in soil, groundwater, crop produce, food chain etc. Thus an experiment was conducted to see persistence of metsulfuron-methyl in paddy field under tropical conditions. Metsulfuron-methyl was applied at 2, 4, 5, and 8 a.i. g ha^{-1} rates after 25 days in transplanted rice as post emergence herbicide. Concentration of metsulfuron-methyl in soil at 30 days was found 0.008, 0.010, 0.011 and 0.016 $\mu g\ g^{-1}$ at 2, 4, 5 and 8 g a.i. ha^{-1} application rates, respectively. However, residue level of metsulfuron-methyl in soil, rice grains and straw at harvest was found below 0.001 $\mu g\ g^{-1}$.

Keywords Metsulfuron-methyl · Residues · Persistence · Paddy field

Herbicides are now extensively used in India. Though they are designed to be biologically active they are often found in soil, plant part and ground water (Xu et al. 2002; Sondhia 2005, 2006, 2008b). Among sulfonylurea herbicides, metsulfuron-methyl [methyl 2-(4-methoxy-6-methyl-1,3,5-triazine-2-ylcarbamoylsulfamoyl) benzoic acid] (Fig. 1) is widely used due to its selectivity against a wide range of weeds in cereal, pasture, and plantation crops (Pons and Barriuso 1998; Sondhia 2008a). Metsulfuron-methyl inhibits acetolactate synthase (ALS) enzyme that catalyzes the first common reaction in the biosynthesis of branched amino acids viz. valine, leucine and isoleucine (Brown and Cotterman 1994). It is used alone or as a mixture to control broad leaf weeds in cereal crops.

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). Soil pH influenced dissipation of sulfonylurea by hydrolysis. The greater the soil pH the less hydrolysis occurs; therefore dissipation in alkaline soil occurs mostly through microbial activity (Sarmah et al. 1998). Although the typical application rate of metsulfuron-methyl to field crops use in the range of 2–12 g a.i. ha^{-1} even though some researcher reported damage to rotation or substitution crops such as sugar beet, maize, cotton, sunflower, soybean and rice seedlings (Junilla et al. 1994; Yao et al. 1997; Nicholls and Evans 1998).

In India, rice is the major food crop in terms of production and consumption which is heavily infested with many broad leaf weeds, and reduces the yield drastically. Metsulfuron-methyl is very effective to control broadleaf weeds. Extensive research has been carried out on mobility, adsorption and persistence of metsulfuron-methyl in upland soil (Pons and Barriuso 1998; Sondhia 2008a). However, little is known about persistence and bioavailability of metsulfuron-methyl in paddy soil. Hence present study was conducted to evaluate the persistence of metsulfuron-methyl in soil and bioaccumulation of residues in paddy under tropical conditions.

S. Sondhia (✉)
National Research Centre for Weed Science, (Indian Council of Agricultural Research), Jabalpur, MP 482004, India
e-mail: shobhasondia@yahoo.com

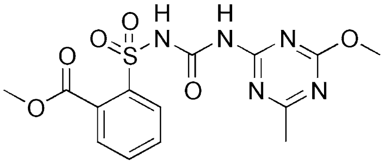

Fig. 1 Chemical structure of metsulfuron-methyl

Materials and Methods

A field experiment was conducted at the experimental field of National Research Centre for Weed Science, Jabalpur, India, in *Kharif* (July to October) 2006 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. Twenty-five days after transplanting of rice plants, four different doses of metsulfuron-methyl (20% WG) viz. 2, 4, 5, and 8 g a.i. ha^{-1} were sprayed as post-emergence herbicide with Knap-sap sprayer using flat fan nozzle. A further three triplicate plots were sprayed with water without any herbicide and maintained as control. The crop was raised as recommended local package of practices. During experimental period crop received approximately 817 mm rainfall and the minimum and maximum temperature was remained 20–32.2°C.

Soil samples were collected at 30, 60, 90 days after application of herbicide and at harvest (115 days). Three kilograms 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. Samples from the control plots were collected before the herbicide treated plots for residue analysis. Soil was clay loam in texture (clay 35.47%, silt 12.34%, and sand 52.19%), nitrogen 305 kg ha^{-1}, phosphorus 42 kg ha^{-1} and available potassium 310 kg ha^{-1} with organic carbon 0.83%, EC 0.36 mmhos cm^{-1} and pH 7.3.

At harvest 500 g of representative rice grains and straw samples were collected from metsulfuron-methyl 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. Samples were stored at −20°C, processed and analyzed within 7 days. Residues analysis was conducted in residue laboratory of National Research Centre for Weed Science, Jabalpur.

Analytical standard of metsulfuron-methyl was purchased from ACCU standard, USA. Other laboratory chemicals and all supplies were obtained from E Merck, Germany.

Metsulfuron-methyl from soil samples (25 g) was extracted as described by Sondhia (2008a). A volume of 20 g representative soil samples were taken in 250 mL Erlenmeyer flask and shaken using a horizontal shaker with deionised water and acetonitrile (4:1) (50 + 30 mL) of for 1 h and filtered through Buchner funnel using water pump. After filtration extract was collected. Extracts were combined and evaporated on a rotary vacuum evaporator to dryness. The residue was dissolved in acetonitrile (5 mL) and filtered through Pall Nylon 0.45 µm filter paper and analyzed by HPLC.

Powdered samples of rice grains (25 g) and straw were taken in 250 mL Erlenmeyer flask, and extracted twice by shaking on a horizontal shaker with deionised water and acetonitrile (4:1) (80 + 50 mL) for 1 h (repeated twice). The contents were filtered, and partitioned with dichloromethane (30 mL). Dichloromethane layer was collected and solvent was concentrated to approximate 5 mL in a rotary vacuum evaporator at 40°C.

Concentrated rice grains and straw extracts were cleaned on glass column (10 cm × 2 cm i.d.) packed with florisil (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. Eluates were collected and solvent was evaporated on a rotary vacuum evaporator to dryness and dissolve in 2 mL acetonitrile.

Metsulfuron-methyl, was analyzed by Shimadzu HPLC Chromatograph consisting LC-10 ATVP pump and SPD-1-AV vp Photo Diode Array (PDA). The HPLC was fitted with a 4.6-mm-diameter × 25-cm-length Phenomenex C_{18} column. The analysis of metsulfuron-methyl was carried out at 220 nm at ambient temperature. Acetonitrile: water (70: 30) was used as mobile phase. The flow rate during elutions was 1 mL min^{-1}. Quantification of herbicides residues was accomplished by comparing the peak area response for samples with peak area of the standards.

To determine method detection limit known concentrations of metsulfuron-methyl (0.001, 0.01, 0.05, 0.1, 0.5 and 5 µg mL^{-1}) were prepared in acetonitrile by diluting the stock solution (1,000 µg mL^{-1}). A volume of 20 µl of the standard solution 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. Ten grams of control samples (soil, rice grain and straw) were taken in 250 mL Erlenmeyer flask and 1 mL of 0.1 and 0.5 µg mL^{-1} standard solution of metsulfuron was added uniformly on the surface of the matrix and extracted as described earlier.

Results and Discussion

The detection limit of metsulfuron-methyl is shown in Table 1. Retention time of metsulfuron-methyl was found to be approximately 2.43 min. Instrumental detection limit for metsulfuron was estimated as described by Sondhia (2008b) and found 0.001 μg g^{-1}. The metsulfuron-methyl recovery varied from 79%–88% and 84%–90% for rice grains and straw samples fortified with 0.1 and 0.5 μg g^{-1} of metsulfuron-methyl, respectively (Table 1). The recoveries of metsulfuron-methyl from soils at different concentration levels were satisfactory being within the range 91%–96%, confirmed a good repeatability of the method (Table 1). The soil blanks did not exhibit any peak interfering with the retention time of metsulfuron-methyl. The equations of analytical calibration graphs, obtained by plotting peak areas in '*y*' axis against concentrations of metsulfuron-methyl in '*x*' axis within the range of 5–0.001 μg mL^{-1} was, $y = 2{,}199{,}374.299x + 453{,}256.1616$, showed good linearity and the value of slope and intercept was 2,199,374 and 4,153,256.2, respectively. The correlation coefficient was 0.99 (Fig. 2).

Results of metsulfuron residues in rice grain and straw as detected by HPLC at various application rates are presented in Table 2. At harvest, metsulfuron-methyl residues in soil, rice grains and straw were below the 0.001 μg g^{-1} in all the treatments showed faster dissipation of metsulfuron-methyl in grain and straw. Residues of metsulfuron-methyl as detected by HPLC in soil are presented in Table 3. Concentration of metsulfuron-methyl in the soil after 30 days was 0.008, 0.010, 0.011 and 0.016 μg g^{-1} at 2, 4, 5 and 8 g a.i. ha^{-1} application rates, respectively. Residues were decreased gradually with the passage of time and by 60 and 90 days residues were found below the detection limit (<0.001 μg g^{-1}) in 2–8 g a.i ha^{-1} application rates (Table 3). In general metsulfuron-methyl dissipated at faster rate in the soil in all the doses and hence could not found after 60 days in soil and at harvest in crop produce.

Table 1 Recovery of metsulfuron methyl-from rice grains and straw

Matrix	Amount added (μg g^{-1})	Amount recovered (μg g^{-1})	Recovery (%)
Rice grains	0.10	0.079 ± 0.005	79
	0.50	0.440 ± 0.010	88
Rice straw	0.10	0.082 ± 0.001	84
	0.50	0.450 ± 0.006	90
Soil	0.10	0.091 ± 0.001	91
	0.50	0.400 ± 0.008	96

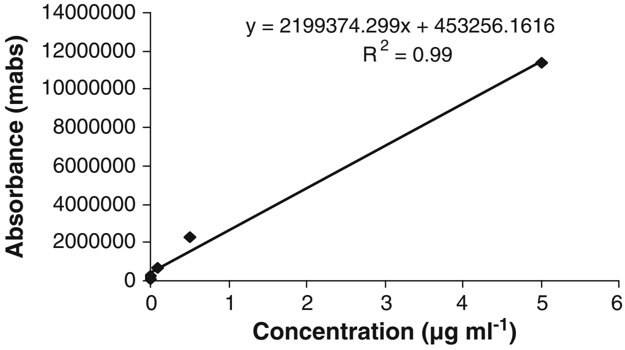

Fig. 2 Calibration of metsulfuron-methyl at 5 to 0.001 μg mL^{-1}

Table 2 Detection of metsulfuron residues in soil, rice grains and straw at harvest

Treatments (g ha^{-1})	Residues (μg g^{-1})		
	Soil	Rice grains	Rice straw
2	BDL	BDL	BDL
4	BDL	BDL	BDL
5	BDL	BDL	BDL
8	BDL	BDL	BDL
Detection limit	0.001	0.001	0.001

BDL Below detection limit

Table 3 Detection of metsulfuron residues in soil

Treatments (g ha^{-1})	Residues (μg $g^{-1)}$		
	Days after application		
	30	60	90
2	0.008 ± 0.001	BDL	BDL
4	0.010 ± 0.012	BDL	BDL
5	0.011 ± 0.007	BDL	BDL
8	0.016 ± 0.012	BDL	BDL
Detection limit	0.001		

BDL Below detection limit

Recently published studies showed that up to 48% of the applied metsulfuron-methyl is converted to bound residues and metabolites in soil (Pons and Barriuso 1998; Ye 2000; Ye et al. 2002). The decrease in the concentration of the pesticide in soil is due to chemical and microbial processes, thereby increasing the rate of dissipation (Sondhia 2008a). 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). 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. Adsorption of sulfonylureas decreases when soil pH increases, due to increase amount of anionic species in solution and thus increases the chance of leaching in deeper soil profile. As absorption of metsulfuron through plant surface is low and hence its bioaccumulation in grain and straw was not found at harvest.

The soil pH also play important role in the degradation of sulfonylurea herbicides (Morrica et al. 2001). As the soil of the experimental field was slightly alkaline (pH 7.3) that may be reason that metsulfuron-methyl was not detected after 60 and 90 days in soil at low application rates. The sulfonylurea group herbicides have low octanal/water partitioning coefficients (K_{ow} value) and relatively higher water solubilities, resulting in a high potential mobility in soils (Sondhia 2008a). Thus in the present study, weak adsorption of metsulfuron-methyl on soil and leaching could also add to the unavailability of metsulfuron-methyl in the surface soil and hence did not accumulate in plant parts.

On the basis of above findings it can be concluded that metsulfuron-methyl application at 2–8 a.i g ha^{-1} can be safely applied to the transplanted rice crop as post-emergence herbicide as residues were found below 0.001 μg g^{-1} at these application rates in soil as well as in crop produce at harvest.

Acknowledgments Author greatly acknowledges Director, National Research Centre for Weed Science (NRCWS), Jabalpur, India for providing necessary facilities to conduct the work and Dr Anil Dixit for agronomical trial.

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