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Persistence of Sulfosulfuron Under Wheat Cropping System

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Abstract Presence of herbicides residue in the soil not only damages the succeeding sensitive crops but also adversely affect human and animal health due to bioaccumulation of residues in crop produce. Thus an experiment was conducted to evaluate persistence of sulfosulfuron residues applied in wheat crop as post-emergence at 25, 50 and 100 g ai ha^{-1} application rates to control weeds. Residues were evaluated in surface and subsurface soil by HPLC using Photo diode array detector. Sulfosulfuron residues were dissipated rapidly in surface and subsurface soil at initial period. After150 days residues were found below 0.001 μg/g in soil samples collected from 25 to 50 g ha^{-1} treated plots. However, at 100 g ha^{-1} dose residues were not detected after 200 days in surface and subsurface soil.

Keywords Sulfosulfuron residues · Persistence · Phytotoxicity · HPLC · Degradation · Wheat

Herbicides are now extensively used in Indian agriculture. Though they are designed to be biologically active, often found in soil, plant part and ground water (Fletcher et al. 1993; Sondhia 2005; Sondhia and Dubey 2006). Sulfosulfuron [1-(4,6-dimethoxypyrimidin-2-yl)-3-(2-ethylsulfonylimadazo [1, 2-α] pyridin-3-yl) sulfonylurea] is a sulfonylurea herbicide of group B. Sulfonylureas are a class of potent herbicides that are characterized as acetolactate synthase-inhibitors (ALS). Due to their high potency, they are typically applied at low rates. This results in lower residue levels in environmental samples as compared to other pesticides. While the level of toxicity to animals from these compounds is low, their ability to persist in soil and water can damage following crops. Sulfosulfuron can be applied pre-emergence or early post-emergence and efficacy can be improved by the addition of adjuvants (Olson et al. 2000). It controls many troublesome grass weeds, including downy brome (*Bromus tectorum* L.), Japanese brome (*Bromus japonicus* Thunb. ex Murr.), cheat (*Bromus secalinus* L.), and ripgut brome (*Bromus rigidus* Roth) (Blackshaw and Hamman 1998; Kelly and Peeper 2003). Sulfosulfuron can also be used for control of volunteer barley (*Hordeum vulgare* L.) in winter wheat.

The increasing use of herbicides may cause environmental problems through offsite transport. Ultimately, leaching and transport of pesticides may not only result in low efficacy, but also in possible groundwater contamination (Faucett et al. 1994). Sulfosulfuron possess high solubility in water, which implies a high potential for movement in soil (Sondhia and Dubey 2006; Sondhia et al. 2007; Fletcher et al. 1994). Leaching is considered as the main cause of groundwater contamination by herbicides (Flury 1996; Sondhia and Dubey 2006; Sondhia 2008). Sulfonylureas are weak acids and they exist primarily in the anionic form in most of the soils. Sulfonylureas are generally weakly adsorbed by soil (Beyer et al. 1988) and degradate through chemical hydrolysis of the sulfonylurea bridge and microbial process. Soil pH, temperature, moisture and organic matter are the major factors that influence sulfonylurea chemical hydrolysis and microbial degradation. Hydrolysis of sulfonylurea in soil is mainly depends on pH (Beyer et al. 1988; Hultgren et al. 2002; James et al. 1999). Greater the soil pH the less hydrolysis

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occurs, therefore the breakdown in alkaline soil is mostly through microbial activity (Sarmah et al. 1998). With increasing pH, sulfosulfuron becomes more soluble hence able to leach from the relatively microbe rich top-soil to deeper in the soil profile where microbial breakdown is less likely to occur.

The impact of persisting herbicide residues on succeeding crops is of great concern as very low concentration can cause crop damage (Miller et al. 1999; Moyer and Hamman 2001; Sondhia et al. 2007). However, only limited research results have been published on biological activity, and persistence of sulfosulfuron in soil under field condition. Thus the objective of this study was to evaluate the potential persistence of sulfosulfuron in surface and subsurface soil which was applied as post-emergence at 25, 50 and 100 g ai ha^{-1} in wheat crop.

Materials and Methods

A field experiment was conducted at the research field of National Research Centre for Weed Science (NRCWS), Jabalpur, India, during 2005–2006 in *Rabi* (winter season) in completely randomized block design (RBD) with three replications to evaluate stability and persistence of the sulfosulfuron residues in soil under wheat based cropping system. Sulfosulfuron was applied as post-emergence herbicide in the wheat crop. Treatments consisted of four doses of sulfosulfuron viz. 0 (T_1), 25 (T_2), 50 (T_3) and 100 g ai ha^{-1} (T_4). Wheat *Cv*. MP-1106 was sown in rows 22.5 cm apart on 25 November, 2005 using seed rate 100 kg ha^{-1} with fertilizer dose of 120 kg N + 60 kg P_2O_5 + 40 kg K ha^{-1}. Sulfosulfuron was applied 30 days after sowing. The herbicide as per treatment was applied in 500 L water ha^{-1} using flat fan nozzle. The crop was raised under irrigated condition with recommended package of practices. Evaluation of persistence of sulfosulfuron residues at various soil depths was conducted in residue laboratory of NRCWS, Jabalpur, India.

To evaluate the persistence of sulfosulfuron residues soil samples were initially collected at 2 h (0 day) and continued on 5, 10, 20, 30, 50, 100, 150, 200, 250, 300 and 365 days after application. At each sampling occasion, soil samples were collected randomly from all the triplicate plots of three different doses and from untreated plot (control) with the help of soil auger from the two depths viz. 0–15 (surface) and 15–30 (subsurface). Pebbles and stones were removed manually, the soil was mixed thoroughly, air-dried, sub sampled (250 g), sieved through 2 mm sieve and used for residues study. The soil characteristic at various depths is given in Table 1.

Table 1 Soil characteristic of the experimental field

Soil depth	Clay (%)	Silt (%)	Sand (%)	OC (%)	pH	EC (m mhos cm^{-1})
0–15	35.47	12.45	52.08	0.80	7.2	0.35
15–30	35.20	12.39	52.41	0.78	7.1	0.33

Soil samples were extracted and analyzed as described by Sondhia and Dubey (2006). Twenty-five grams processed soil sample was weighed in Erlenmeyer flask and extracted with 50 mL of acetonitrile:distilled water (1:1 v/v) using horizontal shaker for 1 h. The samples were filtered in to a round bottom flask. Flask were rinsed with 50 mL of same solvent mixture and filtered. Filtrates were combined and concentrated to approximately 10 mL at 40°C using a rotary vacuum evaporator. The extract was taken in a 125 mL separatory funnel and partitioned with dichloromethane. Dichloromethane layer was collected and subjected to florisil column cleanup and further passed through anhydrous sodium sulfate and activated charcoal. Eluates were collected and passed through 0.20 μm nylon filter paper.

Sulfosulfuron was analyzed by using a Shimadzu High Performance Liquid Chromatograph consisting LC-10 ATvp pump and SPD PDA M10Avp Diode Array detector. A Phenomenex C_{18} column of 25 cm length × 4.6 mm i.d., mobile phase acetonitrile:water (70:30) at a flow rate of 1 mL/min was used. The wavelength was set at 220 nm for detection purpose. Twenty microliters volume of sample and standard were injected using fixed loop Rheodyne injector. At these conditions sulfosulfuron was resolved at 2.30 min. The detection limit of method was 0.001 μg g^{-1} (Fig. 1). At the limit of detection the signal to noise ratio was 3:1. Sulfosulfuron reference analytical standard of purity 99% supplied by Accu, Standard Inc, USA was used in the study. All the other chemicals and solvents were analytical grade supplied by E Merck, Germany.

Different known concentrations of sulfosulfuron (0.001, 0.01, 0.5, 1.0, 5.0 and 10.0 μg mL^{-1}) were 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

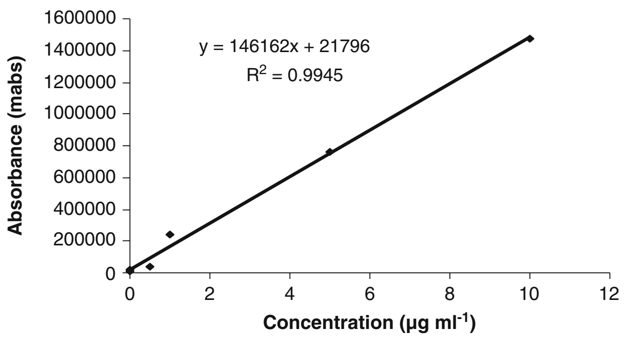

Fig. 1 Calibration of sulfosulfuron at 10–0.001 μg g^{-1} level

terms of recovery studies before analysis of soil samples at each sampling occasion. Ten grams of control sample was taken and 1 mL of 1 and 0.5 μg mL^{-1} standard solution of sulfosulfuron was added uniformly on the surface of the matrix and extracted as described earlier. Recovery of sulfosulfuron was 96% and 94% for the fortification level of 1.0 and 0.5 μg mL^{-1}, respectively. The value of correlation coefficient was 0.99.

Results and Discussion

Analysis of experimental results pertaining to the dissipation of sulfosulfuron in the soil of wheat crop field showed that initial concentration of sulfosulfuron residues were 0.229, 0.967, 1.038 μg g^{-1} in the surface soil (0–15 cm), which dissipated at faster rate to 0.193, 0.274, 0.556 μg g^{-1}, respectively, by 5th days in T_2 (25 g ha^{-1}), T_3 (50 g ha^{-1}) and T_4 (100 g ha^{-1}) treatments. Residues in the subsurface soil (15–30 cm) were found 0.136 μg g^{-1} in T_2, 0.233 μg g^{-1} in T_3 and 0.374 μg g^{-1} in T_4 at 0 days which dissipated to 0.144 μg g^{-1} in T_2, 0.214 μg g^{-1} in T_3 and 0.346 μg g^{-1} in T_4 treatments, by the 5th day. There was gradual decrease of sulfosulfuron residues in the surface and subsurface soil and by 10th day residues in the surface soil were dissipated to 0.089, 0.234 and 0.436 μg g^{-1} in T_2, T_3 and T_4 treatments, respectively. Whereas, sulfosulfuron residues in the subsurface soil depth (15–30 cm) were found 0.086 μg/g in T_2, 0.116 μg g^{-1} in T_3 and 0.154 μg g^{-1} in T_4 treatments.

After 20 days residues got down to 0.082, 0.121, 0.252 μg g^{-1} in T_2, T_3 and T_4 treatments in the surface soil and which further dissipated to 0.068, 0.102, and 0.165 μg g^{-1}, respectively, in T_2, T_3 and T_4 treatments after 30 days. However, 0.040 μg g^{-1} in T_2, 0.114 μg g^{-1} in T_3 and 0.145 μg g^{-1} residues in T_4 treatments were detected in the subsurface soil depth (15–30 cm) after 20 days, which dissipated to 0.033 μg g^{-1} in T_2, 0.091 μg g^{-1} in T_3 and 0.115 μg g^{-1} in T_4 treatments by 30 days. After 50 days 0.038, 0.050 and 0.125 μg g^{-1} sulfosulfuron residues were found in the T_2, T_3 and T_4 treatments, respectively, in the surface soil (0–15 cm). However, residue level of sulfosulfuron in the subsurface soil (15–30 cm) depth was found 0.024 μg g^{-1} in T_2, 0.046 μg g^{-1} in T_3 and 0.105 μg g^{-1} in T_4 after 50 days.

Concentration of sulfosulfuron residues was found 0.003, 0.004 and 0.005 μg g^{-1} in the surface soil (0–15 cm) in T_2, T_3 and T_4 treatments at 100 days. Residues were dissipated to 0.002 and 0.002 μg g^{-1} after 150 days in the T_3 and T_4, respectively, in the surface soil. However, at 150 days residues were below the detection limit (<0.001 μg g^{-1}) in T_2 in subsurface soil. Residues in the subsurface soil (15–30, cm) were found 0.003 μg g^{-1} in T_2, 0.002 μg g^{-1} in T_3 and 0.003 μg g^{-1} in T_4, at 100 days which further dissipated to 0.002 μg g^{-1} at 15–30 cm soil depths in T_3 (50 g ha^{-1}) and 0.002 μg/g in T_4, respectively, by the 150th day. Residues were below the detection limit (<0.001 μg g^{-1}) in both the soil depths (0–15 and 15–30, cm) after 200 days in all the treatments.

Slow dissipation of sulfosulfuron was observed in the surface and subsurface soil at initial period in T_2 treatment. Sulfosulfuron was dissipated about 15.72% and 5.88% from 0–15 and 15–30 cm soil depth after 5 days (Fig. 2). In general dissipation of sulfosulfuron was faster in higher doses (50 and 100 g ha^{-1}) as compared to lower dose (25 g ha^{-1}). Dissipation of sulfosulfuron in 0–15 and 15–30 cm soil depth was 75.88%, 50.21% and 58.21%, 58.82% in T_3 and T_4 treatments, respectively, after 5th day. There was continuous dissipation on later occasion also and by 20, 30 and 50 days 87.49%, 89.45% and 94.83% of sulfosulfuron was dissipated from the 0–15 cm soil in T_3 and T_4, respectively. However, in the 15–30 cm soil depth, 50.21%, 60.94% and 80.25% sulfosulfuron was dissipated after 20, 30 and 50 days in T_3 and T_4, respectively (Fig. 2).

After 100 days, more than 98% of sulfosulfuron dissipated from the 0–15 and 15–30 cm soil in all the treatments. Sulfosulfuron residues dissipated to 100% by 150 days in T_2 and by 200 days in T_3 and T_4, respectively. Sulfosulfuron had a half life of 16.96 and 18.16 in 25 g ai ha^{-1} dose at 0–15 and 15–30 cm soil depth. However, in 50 and 100 g ai ha^{-1} doses the half lives of sulfosulfuron were found 17.88, 19.55 and 16.50 and 18.61 days, respectively, in 0–15 and 15–30 cm soil (Fig. 2).

From the above reported data it appeared that sulfosulfuron residues were dissipated at faster rate at initial period only and by 150 days residues were not found in the T_2 at the detection limit of 0.001 μg g^{-1}, whereas in T_3 and T_4 residues become not detectable after 200 days. This rapid dissipation at initial period is achieved due to hydrolysis of urea bridge, microbial dissipation, leaching, formation of bound residues and metabolites in the soil. Soil pH has a dramatic effect on solubility and hydrolytic breakdown of sulfonylureas herbicides. These herbicides are rapidly degraded in low pH soils by acid hydrolysis and persist for longer period in soils having high pH and clay content (Anderson and Barrett 1985). Therefore, incidences of sulfonylurea injury to following crops are higher in high pH soils. Herbicide persistence is also negatively correlated with temperature (Moyer and Esau 1996) and precipitation. High precipitation and high temperature reduce the chances for herbicide carryover effects, due to higher losses through leaching, microbial degradation, hydrolysis and surface runoff. Therefore, soil pH and climatic conditions in the intervening periods and duration between herbicide application and following crops are important in determining the potential for herbicide carryover.

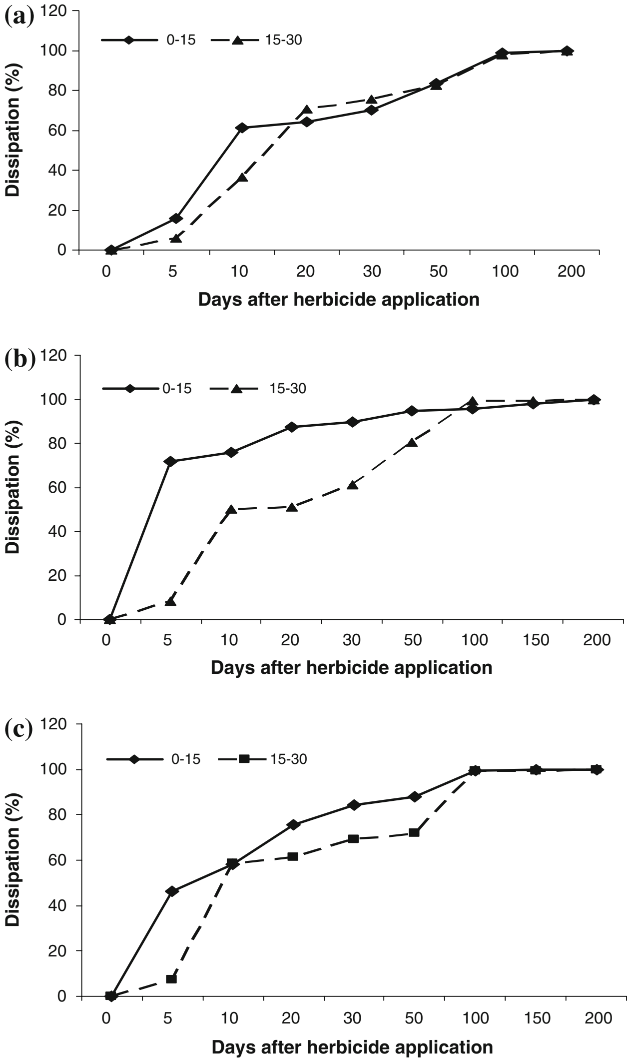

Fig. 2 Dissipation of sulfosulfuron at two depths in 25 (**a**), 50 (**b**) and 100 g ai ha^{-1} (**c**) dose

In the soil the decrease in the concentration of the herbicide in soil is compensated by the increased microbial activity, thereby increasing the rate of dissipation (Shelton and Parkin 1991; Sondhia 2005, 2008). Besides the organic matter, clay content can also play an important role in dissipation of pesticides. In fact, it determines a significantly increase of the microbial biomass (Jenkinson and Ladd 1981). The experimental soil was rich in clay content (35%) that might favoured dissipation of sulfosulfuron in the soil hence residues of sulfosulfuron were dissipated to below the detection limit of 0.001 µg g^{-1} after 100 days in 25 g ai ha^{-1} (T$_2$) and 150 days in 50 g ai ha^{-1} (T$_3$) and 100 g ai ha^{-1} (T$_4$) application rates, respectively.

Overall rate of dissipation of sulfosulfuron was found faster in top soil (0–15 cm) as compared to subsurface soil (15–30 cm). The soil properties also play an important role in the dissipation of herbicides. The topsoil (0–15 cm) was rich in organic carbon which in turn enhanced the microbial dissipation of sulfosulfuron in soil as compared to 15–30 cm soil. The clay content was also high in topsoil as compared to subsurface soil. Both reasons might have played important role in faster rate of dissipation of sulfosulfuron in top soil as compared to subsurface soil.

The soil pH also play important role in the degradation of sulfonylurea herbicides. For acidic herbicides such as sulfonylureas, movement in the soil is closely related to soil solution pH (Martins and Mermoud 1999). The pH of the experimental field soil was 7.1 that may be reason that sulfosulfuron was not detected after 100 and 150 days in low and high application rates. Sulfonylurea herbicides are generally weakly adsorbed by soil. Moreover solubility of sulfosulfuron is high in water, hence able to leach from the topsoil to deeper in the soil profile and thus may not be available in the surface soil (0–15 cm). Eleftherohorinos et al. (2004) showed that persistence of sulfosulfuron is more in sandy loam than in silty clay loam soil. Combination of chemical, biological, physical and environmental factors may operate at different level in influencing the degradation of herbicides. The sulfonylurea group herbicides have low octanal/water partitioning coefficients (K_{ow} value) and relatively higher water solubilities (1,627 ppm at pH 7, Pesticide Manual 2003), resulting in a high potential mobility in soils (Brown 1990).

In the present study, weak adsorption of sulfosulfuron on soil and leaching could also add to the unavailability of sulfosulfuron in the surface soil.

It can be concluded sulfosulfuron may affect the succeeding crop due to presence of residues up to 200 days in higher doses and hence care should be taken to avoid phytotoxicity to succeeding sensitive crops such as pea and lentil (Sondhia 2007).

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