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Bioefficacy and persistence of ethoxysulfuron in rice

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ABSTRACT

Although herbicides provide effective weed control, yet some herbicides pose serious health and environment threats. Ethoxysulfuron [3-(4, 6-dimethoxyoyrimidin-2-yl)-1-(2-ethoxyphenoxysulfonyl) urea] belongs to sulfonylurea group having a toxicity class of III and used as a selective herbicide. It acts by reducing the levels of three branched-chain aliphatic amino acids. Bio-efficacy and persistence of ethoxysulfuron (60 %WG) sprayed at 15, 17.50, 18.75 and 20 g ha-1 doses as post-emergence were evaluated in transplanted rice. Among the herbicides all the herbicidal treatments enhanced the grain yield by 50% over weedy check and were statistically at par with each other. The grain yield of rice crop was the highest under weed free situation followed by almix and ethoxysulfuron application. There were no phytotoxic symptoms of ethoxysulfuron on transplanted rice. Soil and crop samples were analyzed to see persistence of ethoxysulfuron. Residues were found below <0.001 µg g-1 in soil, grains and straw at harvest at 15 to 20 g ha-1 doses, respectively. This showed fast dissipation of ethoxysulfuron in soil and plants and thus do not pose environmental risk at applied rates.

Key words: *ethoxysulfuron, bioefficacy, persistence, soil, grains, straw, residues, bioaccumulation*

Transplanted rice is infested with heterogeneous group of weeds under rainfed shallow lowland, which reduces yield up to 24-48 % (Singh and Bhan, 1986). Rapid expansion of Industries has caused an outflow of farm labour to industrial sites and corresponding increases in wages (Chisaka and Noda, 1983). Use of herbicides offer selective and economical control of weeds right from the beginning, giving crop an advantage of good start and competitive superiority. A number of herbicides like butachlor, pretilachlor, anilofos, etc. been recommended as pre-emergence herbicide for the control of early flushes of grassy weeds in transplanted rice. Weed shift is reported due to continuous use of graminicides like butachlor, anilofos, and pretilachlor in rice (Usui 2001; Prasad *et al.*, 2008). These herbicides though efficient but may not control broad leaved weeds. Therefore, new herbicides are continuously needed for solving emerging new weed problems.

Ethoxysulfuron, chemically known as 3-(4, 6-dimethoxyoyrimidin-2-yl)-1-(2-ethoxyphenoxysulfonyl) urea, is a very effective sulfonylurea herbicide commonly used in rice and cereals as a post-emergence. It has high selectivity and very low mammalian toxicity (Brown and Cotterman, 1994). 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). It was observed that ethoxysulfuron translocated within the plants. After inhibition of plant growth, clorotic patches develop and spread at first acropetally then basipetally. The action of the ethoxysulfuron reaches its conclusion in about 3-4 weeks. Ethoxysulfuron acts by inhibition of the acetolachtate synthetase.

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, Sondhia 2008). Each of these processes can be influenced differently by the environmental conditions, including soil properties. There is increasing concern about the persistence of pesticide residues in soils, crop produce and subsequent contamination of groundwater. 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. Weed infestation primarily

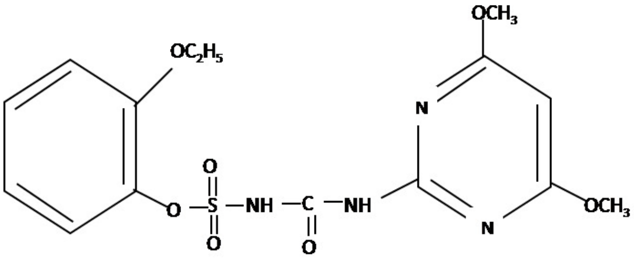

Fig. 1. Chemical structure of ethoxysulfuron [3-(4, 6-dimethoxyoyrimidin-2-yl)-1-(2-ethoxyphenoxysulfonyl) urea

constrain rice production by reducing grain yield by 10-70 per cent depending up on type of weed flora and severity of infestation. In general barn yard grass (*Echinochloa crusgalli*) dominates the rice crop besides some sedges and broadleaved weeds. Excessive use of herbicides could have harmful effects on the environment and might permit some herbicide resistant weeds in cropland. Some authors suggested a potential risk of sulfonylurea herbicides (Fletcher *et al*., 1993; Peterson *et al*., 1994; Sondhia and Singhai 2008; Sondhia 2009), which are active at very low rate of application. Hence present study was conducted to evaluate bioefficacy of and post emergence herbicides and ethoxysulfuron against broad leaved weeds, and sedges in transplanted rice and persistence of ethoxysulfuron, in soil and crop produce at harvest.

MATERIALS AND METHODS

Experiment was conducted during wet season of 2006-07 at the Directorate of for Weed Science Research, Jabalpur. The soil was clay loam, low in available nitrogen, medium in available phosphorus and high in available potassium with neutral pH. Treatments comprised of ethoxysulfuron 60 WG at 15, 17.50 and 20 g a.i ha^{-1}, ethoxysulfuron 15 WG at 18.75 g a.i ha^{-1}, Almix (chlorimuron+metsulfuron) 4g a.i ha^{-1}, 2, 4-D at 500 g a.i ha$^{-1,}$ two hand weeding at 20 and 40 DAT and weedy check. These were applied at 15-20 days after transplanting (DAT), and were replicated three times in a randomized block design. 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 old rice (*Cv*. Kranti) seedlings were transplanted on 16 July, 2006 at 20 x 20 cm spacing. The herbicides were applied in 500 L water ha^{-1} using flat fan nozzle. Crop was raised under irrigated condition with recommended package of practices. Weed population was recorded at 40 DAT and weed dry matter was recorded at 40 DAT. Phyto-toxicity symptoms on crop were noted visually one week after spraying of herbicides. Data on weeds were subjected to square root transformation before analysis. Total rain fall during the crop season was around 950 mm against the average rain fall of 1250 mm.

To see persistence of ethoxysulfuron, soil samples were collected at 60, 90 and 120 days after application of herbicide. Approximately, 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. Soil was sandy 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}, organic carbon 0.80 %, EC 0.35 mmhos cm^{-1} and pH 7.2.

At harvest approximately 500 g of representative rice grains and straw samples were collected from ethoxysulfuron treated and untreated plots. The straw samples were cut into small pieces and air-dried. Rice grains and straw samples were then ground on mechanical grinder and used for residue analysis. Soil samples were stored at –10 ^{0}C, processed and analyzed within seven days. Ethoxysulfuron was extracted and analyzed from crop and soil sample as described by Akiyama *et al*., (2002). Grain, straw and soil samples (25 g) were extracted with acetonitrile: dichloromethane: 1.0 M ammonium hydroxide (30: 8: 2) using horizontal shaker for two hour. The contents were filtered through a Buchner funnel. The extraction was repeated twice (50 + 25 ml). Filtrates were concentrated on rotary vacuum evaporators to about 2 ml.

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 x 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.

Ethoxysulfuron technical grade was obtained from Bayer Crop Science, Mumbai. 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. Ethoxysulfuron residues were analyzed 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-8 (ODS) column (5 ìm particle size, 250 x 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 2.32 min. detection limit of method was 0.001 µg g^{-1}.

RESULTS AND DISCUSSION

Experimental field was infested with mainly broadleaved weeds and sedges were also present in low density. Data on weed population and weed dry weight at 60 days after sowing revealed that application of ethoxysulfuron 60WG at 20 g ha^{-1} reduced the weed population and weed dry weight to a greater extent as compared to other treatments of weed control. Though the application of ethoxysulfuron 15WG at 18.75 g ha^{-1} ha and almix 4g ha^{-1} also recorded the lowest value of weed population and weed dry weight and both were at par to each other. There were no phytotoxic symptoms of ethoxysulfuron on transplanted rice (Table 1 and 2).

Besides *Echinocloa colona*, high intensity of sedges *i.e. Cyperus iria, Cyperus difformis* and specially *Scirpus* spp. were found and among broadleaved weeds *Ammania bacifera*, *Ludwigia Caesulia auxillaris*, *Commelina benghalensis* and *Physalis minima* were predominant and ethoxysulfuron has been found good against these weeds. Bioefficacy of various herbicidal treatments against weeds density, grain yield is presented in Table 1 and 2.

Grain yield of rice crop was highest under weed free situation followed by almix and ethoxysulfuron applications. All the herbicide all the herbicidal treatments enhanced the grain yield by 50% over weedy check and were statistically at par with each other (Table 1).

Table 1. Effect of treatment on weed density, weed biomass and yield of transplanted rice

Treatments	Rate of application (g ha^{-1})	Weed density* (No./m^2)	Weed biomass (g/m^2)	Yield (kg ha^{-1})
Sunrice (ethoxysulfuron) 60WG	15	4.66	56	3850
Sunrice (ethoxysulfuron) 60WG	17. 5	4.59	39	3866
Sunrice (ethoxysulfuron) 60WG	20	3.85	28	3873
Sunrice (ethoxysulfuron) 15 WG	18. 75	4.36	40	3800
Almix (metsulfuron methyl 10% + chlorimurom ethyl 10%) 20WP	2+2	4.09	27	3900
2,4-D EE	500	4.90	33	3683
Two hand weedings/hand hoeing	-	0.71	-	4196
Untreated control	-	7.59	85	2880
LSD (P=0.05)		1.30	12	333

*Weed count values are subjected to square root transformation

Table 2. Effect of sun rice (Ethoxysulfuron 60 WG) on weed density (species wise) in transplanted rice

Treatments	Dose(g ha^{-1})	Weed population (species wise)			
		Casesulia auxillaris	*Commelina benghalensis*	*Alternanthera*	*Cyperus iria*
Sunrice (ethoxysulfuron) 60WG	15	1	1	4	2
Sunrice (ethoxysulfuron) 60WG	17. 5	2	2	4	2
Sunrice (ethoxysulfuron) 60WG	20	2	-	4	1
Sunrice (ethoxysulfuron)15 WG	18. 75	2	2	6	3
Almix (metsulfuron methyl 10% + chlorimurom ethyl 10%) 20WP	2+2	3	1	4	3
2,4-D EE	500	5	3	3	8
Two hand weedings/hand hoeing	-	-	-	-	-
Untreated control	-	20	15	12	9

Ethoxysulfuron dissipates at faster rate in soil and metabolize in rice plants by primary pathway which involves hydroxylation followed by carbohydrate conjugation and cleavage of sulfonylurea linkage.

Residues of ethoxysulfuron were found below <0.001 µg g^{-1} in soil, grains and straw at harvest respectively (Table 3). Ethoxysulfuron dissipates rapidly in soil under aerobic conditions. Hydrolytic dissipation is the major route of ethoxysulfuron degradation in the soil environment. Cleavage of the sulfonylurea linkage yielded 2-ethoxy phenoxy sulfonamide and 4, 6 dimethoxy 2-aminopyrimidine as major dissipation products (Sondhia 2009).

Sulfonylureas degraded slightly faster in/on soil (silty clay loam soil, pH 8) surfaces when exposed to a xenon arc light source [DT_{50} 50 days (light exposed) *vs*. 130 days (dark control)] by cleavage of the sulfonylurea bridge (Rhodes, 1989). Secondary hydrolysis cleavage products were I (2-ethoxyphenoxy sulfonylurea), II (4, 6-methoxy-2-amino-pyrimidine), III (4, 6-hydroxy-aminopyrimidine), and IV (4, 6-dihydroxy -1, 3 pyrimidine). Microbial processes appeared to be most important in the period immediately following application, but then became less important to the dissipation mechanism, especially under field conditions. Minor degradation pathways that involved the intact parent molecule included: hydroxylation of the phenyl-moiety.

In the soil decrease in the concentration of the ethoxysulfuron is compensated by the increased microbial activity, thereby increasing the rate of degradation (Sondhia 2009; Shelton and Parkin, 1991). 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 (Sondhia 2009; Chaussod *et al.*, 1986). The soil was rich in clay content (35 %) that might favoured degradation of ethoxysulfuron in the soil so that by 60 days ethoxysulfuron degraded completely and hence no residues were detected (Table 3). Morrico *et al.*, (2001) and Sondhia and Singhai (2009) also reported rapid dissipation of sulfonylurea herbicides in the field conditions. In the sulfonylurea herbicides, greater adsorption at lower pH has mainly been attributed to adsorption of the molecular forms (Walker *et al* 1989). The pH of the experimental soil was approximately neutral (7.2) which allowed less adsorption of the ethoxysulfuron to the soil and hence residues were not detected after 60 days.

On the basis of above findings it can be concluded that ethoxysulfuron application at 15 - 20 g ha^{-1} can be effectively applied to the transplanted rice crop to control sedges and broadleaved weeds. The aforesaid study revealed that control was effective

Table 3. Detection of ethoxysulfuron residues in soil, grain and straw at harvest

Matrix	Residues (µg g^{-1}) Application rate (g ha^{-1})			
	15.00	17.50	18.75	20.00
Soil	<0.001	<0.001	<0.001	<0.001
Grain	<0.001	<0.001	<0.001	<0.001
Straw	<0.001	<0.001	<0.001	<0.001

when the weeds were 4-6 leaf stage and the control of the weeds significantly improved the grain yield of rice when ethoxysulfuron was applied alone or in combination with fenoxaprop. On the other hand this is also found safe as per residues is concern as at harvest, residues were not detected at these application levels neither in soil nor in crop produce, thus this can be considered as effective and safe herbicide to control sedges and broadleaved weed at 15 to 20 g ha^{-1} in transplanted rice.

REFERENCES

Akiyama Y, Yoshioka N and Tsuji M 2002. Determination of ten sulfonyl urea herbicides in unpolished rice by solid-phase extraction cleanup and LC-diode array detection. Shokuhin Eiseigaku Zasshi. 43(2), 99-103.

Beyer EM, Duffy MF, Hay JV and Schlueter DD 1988. Sulfonylureas: Kearney PC and Kaufman DD [Eds.] Herbicides: Chemistry, Degradation, Mode of Action. Dekker, New York, NY. 3,117-189.

Brown HM and Cotterman JC 1994. Advances in sulfonylura herbicides. In Chemistry of plant protection-herbicides inhibiting branched chain amino acid biosynthesis. (Stetter, J, Eding W (Eds,) Springer-Verleg Berlin Germany, 1994 pp 47-81.

Chaussod R, Nicolardot B, Catroux G and Chre´tien J 1986. Relation entreles caracte´ristiques phisico-chimiques et microbiologiques de quelques sols cultive´s. Science du Sol 2, 213-226.

Chisaka H and Noda K 1983. Farmer weed control technology in mechanized rice system in East Asia, Weed control in Rice, Proceedings of the Conference on Weed Control in Rice: IWSA pg 153-165

Fletcher JS, Pfleeger TG. and Ratsch HC 1993. Potential environmental risks associated with the new sulfonylurea herbicides. Environ Sci Technol 27, 2250- 2252.

Molinari GP, Cavannam S, Bonifacinim F, Giammarustim L and Barefootm AC 1999. Bensulfuron-methyl and metsulfuron-methyl dissipation in water and soil of rice fields. In Proceedings of XI Symposium Pesticide Chemistry, Human and Environmental Exposure to Xenobiotics. (Del Re, A M, Brown C, Errera Evans SP, (Eds) Edizioni La Goliardica-Pavese, Cremona, Italy pp 45-50).

Morrica P, Barbato F, Dello-Iacovo, R, Seccia S and Ungaro F 2001. Kinetics and mechanism of imazosulfuron hydrolysis. J Agril Fd Chem 49, 3816-3820.

Peterson HG, Boutinm C, Martinm PA, Freemarkm KE, Ruecker NJ and Moody MJ 1994. Aquatic phyto-toxicity of 23 pesticides applied at expected environmental concentrations. Aquatic Toxicol 28, 275-292.

Prasad TV, Denesh GR and Kiran VK 2008. Long term effect of herbicides on weed shift and sustainable yields of rice-rice system under lowland conditions in southern Karnataka. Indian J Weed Sci 40 (1&2), 18-21

Rhodes BC 1989. Photo-degradation of [14C] Chlorsulfuron in Arizona Type Soil. DuPont Internal Report, AMR 1563-89.

Shea PJ 1986. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. Weed Sci 34, 474–478.

Singh OP and Bhan VM 1986. Effect of herbicides and water submergence levels on control of weeds in transplanted rice. Indian J Weed Sci 18, 226-230.

Son CY and Rutto KL 2002. Are herbicides essential for paddy control in East Asia? Pakistan J Biol Sci 5, 1352-1362.

Sondhia S 2009. Persistence of metsulfuron-methyl in paddy field and detection of its residues in crop produce. Bull Environ Contam Toxicol 83 (6), 799-802.

Sondhia S 2009. Leaching behaviour of metsulfuron-methyl in two texturally different soil, Environ Monit Assess 154, 111-115

Sondhia S and Singhai B 2008. Persistence of sulfosulfuron under wheat cropping system Bull Environ Contam Toxicol 80(5), 423-427.

Sondhia S 2008. Determination of imazosulfuron persistence in rice crop and soil. Environ Monit Assess 137: 205-211.

Usui K 2001. Metabolism and selectivity of rice herbicides in plants. Weed Biol Manage 1, 137-146.

Walker A, Cotteril EG and Welch SJ 1989. Adsorption and degradation of chlorsulfuron and metsulfuron methyl in soils from different depths. Weed Res 29, 281-287.