Journal of Zhejiang University SCIENCE B
ISSN 1673-1581 (Print); ISSN 1862-1783 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Laboratory simulated dissipation of metsulfuron methyl and chlorimuron ethyl in soils and their residual fate in rice, wheat and soybean at harvest

SANYAL Nilanjan[1], PRAMANIK Sukhendu Kumar[1], PAL Raktim[2], CHOWDHURY Ashim[†3]

([1]*Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741 252, Nadia, West Bengal, India*)

([2]*Institute of Environmental Studies and Wetland Management, B-4, LA–Block, Salt Lake City, Kolkata 700 098, India*)

([3]*Department of Agricultural Chemistry and Soil Science, Calcutta University, Calcutta 700 019, India*)

[†]E-mail: ashimkly@hotmail.com

Received Nov. 22, 2005; revision accepted Jan. 3, 2006

Abstract: Two sulfonylurea herbicides, metsulfuron methyl (Ally 20 WP) and chlorimuron ethyl (Classic 25 WP) were evaluated for their dissipation behaviour in alluvial, coastal saline and laterite soils under laboratory incubated condition at 60% water holding capacity of soils and 30 °C temperature was maintained. In field study herbicides were applied twice for the control of grasses, annual and perennials broad leaves weeds and sedges in rice, wheat and soybean to find out the residual fate of both the herbicides on different matrices of respective crops after harvest. Extraction and clean up methodologies for the herbicides were standardized and subsequently analyzed by HPLC. The study revealed that the half-lives of metsulfuron methyl and chlorimuron ethyl ranged from 10.75 to 13.94 d irrespective of soils and doses applied. Field trials with rice, wheat and soybean also revealed that these two herbicides could safely be recommended for application as no residues were detected in the harvest samples.

Key words: Sulfonylurea, Metsulfuron methyl, Chlorimuron ethyl, Persistence, Harvest, Residue
doi:10.1631/jzus.2006.B0202 **Document code:** A **CLC number:** S13; S482.4

INTRODUCTION

India is a leading producer of rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.) and soybean (*Glycine max* L.) in the world. In every year most of the yields are losses due to the infestation of grass, annual and perennials broad leaves weeds and sedges. There are many herbicides to control these weeds, among them metsulfuron methyl [2-(4-methoxy-6-methyl-1, 3,5-triazin-2-yl-carbamoylsulfamoyl) methyl benzoate] and chlorimuron ethyl [2-(4-chloro-6-methoxy pyrimidin-2-yl-carbamoylsulfamoyl) ethyl benzoate] are selective pre-emergence and post-emergence sulfonylurea herbicides, used primarily to control broadleaf weeds and some grasses. It was already established that sulfonylurea group of herbicides are very effective against various weeds and grasses (Suzuki *et al*., 1990; Umehara and Suzuki, 1992; Hamada *et al*., 1999; Chu *et al*., 2002). In recent years a number of field trials of metsulfuron methyl and chlorimuron ethyl were reported in various crops viz. wheat, barley, maize and soybean (Nazarova *et al*., 1991; He, 1993; Liu *et al*., 1993; Molinari *et al*., 1998). Metsulfuron methyl is rapidly taken up in plant system by roots and by foliage as well. The chemical is translocated throughout the plant, but is not persistent. It is broken down into non-herbicidal products in tolerant plants (Anonymous, 1996a). But there is no systemic study on harvest time residues of metsulfuron methyl and chlorimuron ethyl in rice, wheat and soybean under Indian agro-climatic condition.

Crops in the present experiment are being cultivated widely throughout India under different types of soils having diverse physiochemical properties.

The breakdown of metsulfuron methyl in soils is largely dependant on soil temperature, moisture content, organic matter and pH. The chemical will degrade faster under acidic conditions, and in soils with higher moisture content at higher temperature (Smith, 1986). The chemical has higher mobility potential in alkaline soils than in acidic soils, as it is more soluble under alkaline conditions. Half-life estimates for metsulfuron methyl in soil are wide, ranging from 14~180 d, with an overall average of reported values of 30 d (Anonymous, 1996a). Field dissipation half-life of nicosulfuron was 3 weeks at pH 6.5, 7 weeks at pH 7.4, and 2 weeks at pH 8 and the half-life in silt clay soil is 26 d (Anonymous, 1995). Reported field half-lives of sulfometuron methyl range from 20 to 28 d (Wauchope *et al*., 1992). Primisulfuron methyl is of low to moderate persistence in the soil environment, with a field half-life of from 4 to 60 d, average value of 30 d (Anonymous, 1996b). Rimsulfuron hydrolyses rapidly in soil under conditions of high temperature and low pH. In laboratory tests performed on a sandy loam soil (pH 6.3), half-lives of 24.5 and 22.5 d under anaerobic and aerobic conditions, respectively, have been observed. On the other hand in field experiments on a Danish light sandy soil, half-lives of 90 and 120 d for split treatment and single herbicide application, respectively have been found (Vischetti *et al*., 2000). But there is no information related to the dissipation of chlorimuron ethyl in soil either under laboratory condition or in field. These reports indicate the link between persistence of sulfonylurea herbicides in soil and soil physicochemical properties and also point to the possibility of a large range of half-lives depending on climatic conditions.

Most dissipation studies on pesticide applications were carried out in non-problem soils. There are few such studies on a large part of arable soils, which are either naturally or anthropologically saline and are problem soils. Detailed review of available literature revealed several reports on the persistence and dissipation behavior of sulfonylurea herbicides in different soils other than Indian soils. With these basic information, a laboratory simulated study was simultaneously undertaken to evaluate the effect of soils from different agro-climatic zones of West Bengal, India on the dissipation pattern of metsulfuron methyl and chlorimuron ethyl, and at the same time an attempt was also made to evaluate the residual fate of these herbicides under field conditions in some important crops.

MATERIALS AND METHODS

Field study with rice, wheat and soybean

Field experiments for consecutive three seasons [Season I, 2000; Season II, 2001; Season III, 2002] were laid out with rice (variety “IR-36”), wheat (variety “Sonalika”) and soybean (variety “Bragg”) in a randomized block design (RBD), replicated thrice for metsulfuron methyl and chlorimuron ethyl in 5 m×4 m plots at the University Research Farm, Bidhan Chandra Krishi Viswavidyalaya, Kalyani, Nadia, West Bengal.

Metsulfuron methyl (Ally 20 WP) was applied twice in 5 d interval at a recommended dose of 4 g a.i./ha (T_1) and double the recommended dose of 8 g a.i./ha (T_2) and chlorimuron ethyl (Classic 25 WP) was also applied twice in 5 d interval at recommended dose of 6 g a.i./ha (T_1) and double the recommended dose of 12 g a.i./ha (T_2). In both cases an untreated control (T_3) was maintained.

For harvest time residue grain, straw and soil samples cropped with rice and wheat and for soybean pod and soil were collected (using random sampling technique) from replicated treatment plots and samples from control plots were taken similarly.

Laboratory incubation study with soils

Three different agricultural soils were used in this study viz. alluvial soil (Soil A), coastal saline soil (Soil B) and laterite soil (Soil C). Samples of Soil A were collected from the surface layer (0~15 cm) at the Experimental Farm of Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India. The soil was a typic udifluvent (USDA classification) of clay loam texture with 36.6% clay content and the main characteristics of the top 15 cm were: 0.99% organic C, 0.09% total N, pH 7.2, electrical conductivity 0.81 (dS/m) and cation exchange capacity 15.9 cmol (p^+)/kg. Soil B was collected from the surface layer (0~15 cm) at the Agricultural Experimental Farm of Central Soil Salinity Research Institute, Canning Town, West Bengal, India. The soil was a typic endoaquept (USDA classification) of clay loam texture with 29% clay content and the main characteristics of the top 15 cm were: 1.03% organic C, 0.096% total N, pH 7.2, electrical conductivity 5.3 (dS/m) and cation exchange capacity 8.80 cmol (p^+)/kg. Soil C was collected from the surface layer (0~15 cm) at the Agricultural Experimental Farm of Bidhan Chandra Krishi Viswavidyalaya, Jhargram, West Bengal, India. The soil was a typic haplustalf (USDA classification) of clay loam texture with 13% clay content and the main characteristics of the top 15 cm were: 0.51% organic C, 0.05% total N, pH 5.1, electrical conductivity 0.083 (dS/m) and cation exchange capacity 2.79 cmol (p^+)/kg. The soils had no history of receiving any pesticide treatment 6 months prior to this study.

The two herbicides (metsulfuron methyl and chlorimuron ethyl) were applied to the soil at recommended dose and double the recommended dose. The conversion of the field application to mg of the herbicides per kg of soil was calculated assuming an even distribution of the herbicides in the 0~15 cm layer. The incubation study was carried out at 60% of maximum water holding capacity of the soil and the moisture content of the soils was maintained with the aseptic addition of sterile distilled water. The calculated amount of the sterile (passed through 0.2 μm membrane filter paper) solution of the herbicides in 1 ml acetone was applied to 50 g soil in individual amber coloured Erlenmeyer flasks (250 ml) plugged with cotton pad. After complete removal of acetone by evaporation at room temperature, the flasks were incubated at 30 °C for the periodic incubation study at intervals of day 0, 5, 10, 20, 30, 45 and 60. The control samples received only acetone but underwent the same procedure.

Extraction and cleanup

For extraction and cleanup, samples treated with metsulfuron methyl representative amount of soil samples (100 g) cropped with rice, wheat and soybean at harvest were dissolved overnight with a mixture (100 ml) of acetonitrile and Buffer-A (0.82 g of sodium acetate and 0.5 ml of glacial acetic acid were dissolved in 1 L of distilled water) at ratio of 4:1 (*V*/*V*). It was shaken for 2 h in a mechanical shaker and laid aside for flocculation of soil particles. The supernatant was filtered through a Buchner funnel using (50 ml+50 ml) acetonitrile as washing solvent. The combined filtrate was then concentrated under vacuum at 40 °C and thus taken for cleanup.

The grain and chopped straw samples (50 g) of rice, wheat and the representative amount of chopped pod and seed samples (50 g) of soybean were extracted with 100 ml of acetonitrile and Buffer-A (8:2, *V*/*V*) in a warring blender and filtered through a Buchner funnel using (50 ml+50 ml) acetonitrile as washing solvent. The combined filtrate was concentrated using rotary vacuum evaporator and ready for cleanup.

The concentrated extract obtained from the extraction procedure was transferred to separating funnel with 20 ml of Buffer-B (10.8 g sodium bi-carbonate and 21.1 g of sodium carbonate was dissolved in 2 L of distilled water) and partitioned thrice with dichloromethane (100 ml+50 ml+50 ml). The organic layer was discarded and the pH of the aqueous layer was adjusted to 3.5 with hydrochloric acid (10%). The aqueous fraction was further partitioned with toluene (100 ml+50 ml+50 ml) and the organic phase was collected over anhydrous sodium sulphate. The combined organic fraction was concentrated and subjected to chromatography in column (25 cm×2.5 cm) over silica gel (60~100 mesh) with anhydrous sodium sulphate at the top as adsorbent. The column was first eluted with 75 ml of benzene followed by 75 ml mixture of benzene and methanol (1:1, *V*/*V*) and the whole were discarded. Finally the column was eluted with mixture of 750 ml cyclohexane:125 ml isopropanol:125 ml CH_3OH:1 ml glacial acetic acid. The eluate was collected and evaporated and reconstituted with 10 ml of acetonitrile:water (7:3, *V*/*V*) of HPLC grade for final analysis.

Chlorimuron ethyl soil samples (100 g) collected for treatment and dissolved overnight with mixture (100 ml) of methanol and Buffer-C (0.1 mol/L sodium carbonate and 0.1 mol/L sodium bi-carbonate (pH 10)) at ratio of 1:1 (*V*/*V*) were shaken vigorously for 2 h and kept aside for flocculation of soil particles. Then the supernatant was filtered through a Buchner funnel using (50 ml+50 ml) methanol as washing solvent. The total filtrate was concentrated in a rotary vacuum evaporator at 40 °C. The pH of the aqueous phase was adjusted to 3.0 by sulfuric acid (5%). Since at this pH chlorimuron ethyl exists in the nonionic form and can be extracted by organic solvent.

The grain, seed, and chopped straw and pod samples (50 g each) were dissolved with the mixture of dichloromethane and water (3:1, *V*/*V*). Then it was blended and filtered. The filtrates were combined and concentrated under vacuum for cleanup.

The aqueous extract thus obtained from extraction procedure was partitioned thrice with *n*-hexane (100 ml+50 ml+50 ml) and the aqueous layer was discarded. The aqueous fraction was further partitioned thrice with dichloromethane (100 ml+50 ml+50 ml) and the organic layer was collected over anhydrous sodium sulphate. The combined fraction was concentrated and subjected to chromatography over florisil. The column was eluted with 50 ml methanol followed by 50 ml mixture of methanol and water (7:3, *V*/*V*) and both solvents were discarded. Finally the column was eluted with 150 ml acetonitrile and the eluate was collected and evaporated to dryness under reduced pressure and reconstituted with 10 ml mixture of acetonitrile and water (7:3, *V*/*V*) of HPLC grade for analysis.

Analysis of metsulfuron-methyl and chlorimuron ethyl in rice, wheat and soybean at harvest were conducted in HPLC (Hewlett Packard Liquid Chromatograph Model HP 1050) equipped with Shandon Hypersil HPLC Column 250 mm×46 mm ODS-5 μm (RPC_{18}). HPLC grade acetonitrile and water mixture (7:3, *V*/*V*) was used as mobile phase. HPLC was coupled with UV/VIS detector and the absorption maxima (μ_{max}) were fixed at 254 nm and 235 nm for metsulfuron methyl and chlorimuron ethyl respectively.

The same methodologies for extraction and cleanup process were adopted for laboratory simulated soil dissipation study described for field soils.

Recovery study

In order to establish the efficiency of the method employed for extracting metsulfuron methyl and chlorimuron ethyl from grain, straw, pod, seed and soil samples respectively, sample matrices were spiked with 1.0×10^{-6}, 0.5×10^{-6} and 0.25×10^{-6} analytical standard of metsulfuron methyl and chlorimuron ethyl respectively. The average recoveries for metsulfuron methyl and chlorimuron ethyl are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

Harvest time residues in rice, wheat and soybean

In the present studies the time gap between the last application of the herbicides and harvest was 10~12 weeks. Tables 3 and 4 show that at the harvested matrices of rice, wheat and soybean, there were no residues of metsulfuron methyl and chlorimuron ethyl, which is in accordance with the previous report (Anonymous, 1996a).

Dissipation in soil

The dissipation parameters ($t_{1/2}$) reported in Tables 5 and 6 were calculated from the best fit lines of the logarithm of residual concentration versus time for soil at both levels of treatments suggested that dissipation of chlorimuron ethyl and metsulfuron methyl followed first order kinetics (r>0.94).

Initial deposits in soils immediately after application (zero day) were 0.028 to 0.074 mg/kg (for chlorimuron ethyl) and 0.019 to 0.039 mg/kg (for

Table 1 Recovery of metsulfuron methyl from different substrates

Amount fortified (mg/kg)	Percent recovered								
	Rice			Wheat			Soybean		
	Grain	Straw	Soil	Grain	Straw	Soil	Pod	Seed	Soil
1.00	89.5	85.4	90.1	91.7	86.5	92.0	86.4	83.6	89.5
0.50	88.7	87.6	86.3	92.1	86.4	87.4	89.7	85.0	84.3
0.25	84.8	85.7	85.2	82.4	90.6	86.0	88.1	84.7	81.8

Table 2 Recovery of chlorimuron ethyl form different substrates

Amount fortified (mg/kg)	Percent recovered								
	Rice			Wheat			Soybean		
	Grain	Straw	Soil	Grain	Straw	Soil	Pod	Seed	Soil
1.00	82.3	90.5	83.9	85.1	91.3	81.4	87.2	85.7	84.3
0.50	84.3	82.0	85.6	83.6	86.4	84.1	83.2	88.4	87.2
0.25	88.5	84.2	87.3	86.7	84.6	85.3	88.3	83.6	89.4

metsulfuron methyl) respectively for lower and higher rates respectively. Dissipation rate constant (d^{-1}) of chlorimuron ethyl ranged from 0.0219~0.0248 (Soil A), 0.0255~0.0266 (Soil B) and 0.0270~0.0280 (Soil C) whereas that for metsulfuron methyl were 0.0216~0.0222 (Soil A), 0.0219~0.0231 (Soil B) and 0.0230~0.0241 (Soil C). In most cases, the higher the application rates of the herbicide, the higher were the dissipation rate constants. In general the herbicides persisted for 45 to 60 d irrespective of the treatment combinations. The half-lives of chlorimuron ethyl ranged from 12.14~13.75 d (Soil A), 11.32~11.81 d (Soil B) and 10.75~11.15 d (Soil C) while that for metsulfuron methyl treated soils varied from 13.68~13.94 d (Soil A), 13.03~13.75 d (Soil B) and 12.49~13.09 d (Soil C). Dissipation pattern of both herbicides followed similar trend and half-lives obtained within 14 d irrespective of soils, which accorded well with previous report (Anonymous, 1996a). Thus initial concentrations produced a

Table 3 Harvest time residues of metsulfuron methyl in rice, wheat and soybean

Season	Treatment	Residues (mg/kg)								
		Rice			Wheat			Soybean		
		Grain	Straw	Soil	Grain	Straw	Soil	Pod	Seed	Soil
I	T_1 (4 g a.i./ha)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
II		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
I	T_2 (8 g a.i./ha)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
II		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL: Below detectable limit

Table 4 Harvest time residues of chlorimuron ethyl in rice, wheat and soybean

Season	Treatment	Residues (mg/kg)								
		Rice			Wheat			Soybean		
		Grain	Straw	Soil	Grain	Straw	Soil	Pod	Seed	Soil
I	T_1 (4 g a.i./ha)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
II		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
I	T_2 (8 g a.i./ha)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
II		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL: Below detectable limit

Table 5 Dissipation of chlorimuron ethyl in alluvial, coastal saline and laterite soils

Soil	Dose	Residues remaining in soil (mg/kg)* [% dissipation]							Regression equation
		0	5	10	20	30	45	60	[$t_{1/2}$ (d)]
A	T_1	0.029±0.005	0.021±0.001 [27.60]	0.017±0.002 [41.40]	0.014±0.001 [51.70]	0.007±0.001 [75.80]	0.003±0.001 [90.60]	BDL	Y=1.4749−0.0219X [13.75]
	T_2	0.072±0.008	0.056±0.004 [22.00]	0.048±0.005 [33.00]	0.035±0.006 [51.40]	0.018±0.001 [75.00]	0.005±0.001 [93.00]	BDL	Y=1.9184−0.0248X [12.14]
B	T_1	0.031±0.003	0.020±0.001 [35.69]	0.015±0.006 [51.06]	0.009±0.002 [69.55]	0.005±0.001 [83.97]	BDL	BDL	Y=1.4583−0.0255X [11.81]
	T_2	0.074±0.004	0.045±0.006 [39.19]	0.038±0.002 [48.68]	0.028±0.001 [61.61]	0.016±0.005 [78.32]	0.004±0.003 [95.18]	BDL	Y=1.8739−0.0266X [11.32]
C	T_1	0.028±0.002	0.019±0.001 [31.12]	0.016±0.006 [43.67]	0.011±0.002 [59.71]	0.006±0.006 [79.98]	0.001±0.003 [95.29]	BDL	Y=1.4878−0.0280X [10.75]
	T_2	0.072±0.004	0.051±0.005 [29.05]	0.042±0.002 [41.11]	0.035±0.002 [50.89]	0.016±0.006 [78.01]	0.004±0.003 [94.81]	BDL	Y=1.9128−0.0270X [11.15]

* Mean of three replications; BDL: Below detectable limit

Table 6 Dissipation of metsulfuron methyl in alluvial, coastal saline and laterite soils

Soil	Dose	Residues remaining in soil (mg/kg)* [% Dissipation]							Regression equation
		0	5	10	20	30	45	60	[$t_{1/2}$ (d)]
A	T_1	0.022±0.005	0.015±0.001 [31.80]	0.014±0.002 [36.40]	0.011±0.001 [50.00]	0.006±0.001 [72.70]	0.002±0.001 [90.40]	BDL	Y=1.3607−0.0216X [13.94]
	T_2	0.038±0.008	0.025±0.004 [34.20]	0.022±0.005 [42.10]	0.018±0.006 [52.60]	0.008±0.001 [78.40]	0.003±0.001 [91.10]	BDL	Y=1.5777−0.0222X [13.68]
B	T_1	0.021±0.003	0.012±0.001 [42.86]	0.009±0.006 [57.14]	0.007±0.002 [66.67]	0.004±0.001 [81.43]	BDL	BDL	Y=1.2435−0.0219X [13.75]
	T_2	0.039±0.004	0.022±0.006 [43.59]	0.018±0.002 [53.85]	0.013±0.001 [66.67]	0.010±0.005 [75.13]	0.003±0.003 [93.33]	BDL	Y=1.5407−0.0231X [13.03]
C	T_1	0.019±0.002	0.013±0.001 [33.20]	0.012±0.006 [37.60]	0.009±0.002 [54.70]	0.005±0.006 [76.80]	0.001±0.003 [93.01]	BDL	Y=1.3209−0.0241X [12.49]
	T_2	0.039±0.004	0.024±0.005 [36.72]	0.022±0.002 [43.23]	0.017±0.002 [55.39]	0.009±0.006 [75.91]	0.003±0.003 [92.41]	BDL	Y=1.5877−0.0230X [13.09]

* Mean of three replications; BDL: Below detectable limit

positive effect on half-lives in Soils A and B, which decreased with higher rates of application. In contrast, Soil C showed the opposite result and had the lowest half-lives for both the herbicides. Smith (1986) reported that metsulfuron methyl degrades faster under acidic soils. In the present study Soil C had acidic pH and lowest organic C content. Organic matter lowers the pesticide degradation by adsorption processes (Pal *et al*., 2005). Thus lowest pH and least organic C content in Soil C might be responsible for the lowest half-lives compared to Soils A and B. Dissipation of the herbicides was generally slower in Soil B than in Soil C and faster compared to Soil A, which seemed to be related to soil salinity. In a study using parathion, which is of different molecular nature, was found to be more stable in saline environment than in non-saline environment (Reddy and Sethunathan, 1985). Thus it seemed that the dissipation rates of pesticides in saline environment depend upon the nature of the molecule. The dissipation pattern of chlorimuron ethyl followed similar trend irrespective of soils, which might be due to the similarities in the nature of the molecule of metsulfuron methyl.

Results of the controlled laboratory studies cannot be reliably extrapolated to field conditions and field studies will be a more realistic approach.

ACKNOWLEDGEMENT

The authors are grateful to the Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, India for providing the necessary instrumental facilities.

References

Anonymous, 1995. Extension Toxicology Network, Pesticide Information Profiles. Oregon State University. http://extoxnet.orst.edu/pips/nicosulf.htm. Last updated on May, 1995, accessed on Oct. 15, 2005.

Anonymous, 1996a. Extension Toxicology Network, Pesticide Information Profiles. Oregon State University. http://extoxnet.orst.edu/pips/metsulfu.htm. Last updated on Oct., 1996, accessed on Oct. 15, 2005.

Anonymous, 1996b. Extension Toxicology Network, Pesticide Information Profiles. Oregon State University. http://extoxnet.orst.edu/pips/metsulfu.htm. Last updated on June, 1996, accessed on Oct. 15, 2005.

Chu, C., Lin, H.T., Wong, S.S., Li, G.C., 2002. Distribution and degradation of pyrazosulfuron-ethyl in paddy field. *Plant Prot. Bull. Taipei*, **44**:147-156.

Hamada, M., Wakayama, K., Matsumoto, N., Kamatani, H., Nawamaki, T., 1999. Development of water dispersible granules of cafenstrole and pyrazosulfuron-ethyl mixture as a rice herbicide formulation and its application technology. *J. Weed Sci. Tech.*, **44**:377-382.

He, J.H., 1993. Field experiments of residue effects of metsulfuron-methyl and chlorfuron [chlorsulfuron] applied to wheat or barley on their subsequent crops of spring maize or spring soybean. *Zhejiang Nongye Kexue*, **2**:94-97.

Liu, Z.J., Chen, D.W., Jiang, M.G., Liu, Z.J., Chen, D.W., Jiang, M.G., 1993. A study on residue determination and degradation of metsulfuron herbicide in wheat field soil. *J. Nanjing Agr. Univ.*, **16**:96-99.

Molinari, G.P., Cavanna, S., Freschi, G., Bonacini, F., Giammarrusti, L., 1998. Dissipation in Paddy Water and Soil of Bensulfuron-Methyl and Metsulfuron-Methyl: Preliminary Results. Proc. Giornate Fitopatologiche, Scicli e Ragusa, Italy, p.47-52.

Nazarova, T.A., Makeev, A.M., Chkanikov, D.I., 1991. Residues of chlorsulfuron in the grain and straw of wheat and barley. *Agrokhimiya*, **7**:86-89.

Pal, R., Chakrabarti, K., Chakraborty, A., Chowdhury, A.,

2005. Pencycuron application to soils: degradation and effect on microbiological parameters. *Chemosphere*, **60**(11):1513-1522. [doi:10.1016/j.chemosphere.2005.02.068]

Reddy, B.R., Sethunathan, N., 1985. Salinity and the persistence of parathion in flooded soil. *Soil Biol. Biochem.*, **17**:235-239.

Smith, A.E., 1986. Persistence of the herbicides [14C] chlorsulfuron and [14C] metsulfuron-methyl in prairie soils under laboratory conditions. *Bull. Environ. Contam. Toxicol.*, **37**(1):698-704. [doi:10.1007/BF01607826]

Suzuki, K., Shirai, Y., Hirata, H., 1990. New Sulfonylurea Herbicide for Paddy Rice. *In*: Graysan, B.T., Green, M.B. (Eds.), Pest Management in Rice. Society of Chemical Industry, London, UK, p.238-348.

Umehara, T., Suzuki, K., 1992. Development of paddy herbicide, pyrazosulfuron-ethyl (NC-311). Proc. 1st Int. Weed Control Cong. The University of Queensland, Australia, p.527-529.

Vischetti, C., Perucci, P., Scarponi, L., 2000. Relationship between rimsulfuron degradation and microbial biomass content in a clay loam soil. *Biol. Fertil. Soils*, **31**(3-4):310-314. [doi:10.1007/s003740050661]

Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., Burt, J.P., 1992. Pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.*, **123**:1-157.