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Persistence of the Herbicides [14C]Chlorsulfuron and [14C]Metsulfuron Methyl in Prairie Soils under Laboratory Conditions

Allan E. Smith

Agriculture Canada, Research Station, Box 440, Regina, Saskatchewan,
Canada, S4P 3A2

Metsulfuron methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate), whose structure is closely related to that of chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide), is currently being evaluated on the Canadian prairies as a postemergence treatment for the control of broadleaf weeds in cereal crops, in non-crop land and for brush control.

Although applied postemergence, some of the herbicide will come into contact with the soil making it necessary to determine the fate of metsulfuron methyl in the soil. It has been noted (Joshi and Brown 1985) that the herbicide undergoes degradation by both biological and chemical mechanisms. Soil temperature, soil moisture and soil pH also affect the rate of degradation with dissipation being greater in acidic soils than in alkaline. In this regard, metsulfuron methyl is similar to chlorsulfuron which undergoes degradation in the soil by a combination of chemical and biochemical hydrolyses that are dependent upon soil temperature and water content and soil pH (Anderson and Barrett 1985; Joshi et al. 1985; Thirunarayanan et al. 1985; Walker and Brown 1983).

The pKa of metsulfuron methyl is 3.7 and the water solubility at pH 5 is 0.27 mg/mL, whereas at a pH of 7, where the molecule exists in the ionized form, the solubility is 9.5 mg/mL (Anon. 1984). Chlorsulfuron, with a pka of 3.7, has low soil adsorptive properties and undergoes leaching (Mersie and Foy 1985; Shea 1982; Thirunarayanan et al. 1985).

These studies were undertaken to investigate the rate of breakdown and the fate of [14C]metsulfuron methyl in three soils under laboratory conditions where no leaching could occur. The rate of breakdown of [14C]chlorsulfuron was also investigated in one of the soils.

MATERIALS AND METHODS

The composition and physical properties of the clay, clay loam and sandy loam used in these studies have already been described (Smith and Muir 1980), the pH values of the soils were 7.5, 5.2

and 6.8, respectively. Samples of all soils were collected from the surface 5-cm horizons during September, 1984 when the moisture contents were below 10% of their field capacities. The soils were screened through a 2-mm sieve and stored at laboratory temperature until the studies were commenced in November, 1984.

[14C]Chlorsulfuron and [14C]metsulfuron methyl, both labeled in the phenyl ring and with radiochemical purities of over 99.5%, were provided by E.I. du Pont de Nemours & Co., Wilmington, DE. The former compound had a specific activity of 6.01 uCi/mg, while the activity of the latter was 8.62 uCi/mg. The radioactive herbicides were dissolved in methanol to yield solutions containing 0.333 mg/mL and 0.468 mg/mL chlorsulfuron and metsulfuron methyl, respectively. Analytically pure samples of chlorsulfuron, metsulfuron methyl, 2-chlorobenzenesulfonamide and 2-carboxymethylbenzenesulfonamide were also provided by E.I. du Pont de Nemours for chromatographic purposes. Individual solutions of all non-radioactive compounds were prepared in acetone, at concentrations of 1 mg/mL.

Samples (50 g) of the clay, clay loam and sandy loam at 85% of their field capacities were weighed into 175-mL polystyrene foam containers fitted with plastic lids and incubated in the dark at 20C for 7 days. Distilled water was added (by weight) every second day to maintain the moisture contents. After equilibration, 14 cartons containing clay were treated with [14C]chlorsulfuron solution (70 uL, 0.14 uCi, 23.3 ug herbicide). An additional 14 containers of the moist clay were similarly treated with with [14C]metsulfuron methyl (50 uL, 0.20 uCi, 23.4 ug herbicide). Twelve cartons of the clay loam and sandy loam were also treated with the same amounts of [14C]metsulfuron methyl. The soil concentration of both chemicals was 0.47 ug/g, based on moist soil. Following treatment, the soils were thoroughly mixed and the capped cartons incubated in the dark at 20°C. Water was added, with mixing, every second day to maintain water content.

Duplicate samples of the clay treated with chlorsulfuron and metsulfuron methyl were extracted and analyzed radiochemically after 1 h and then after 7, 14, 28, 49, 70 and 98 days. Duplicate samples of the clay loam and sandy loam treated with metsulfuron methyl were extracted and analyzed after 1 h and then after 7, 14, 28, 56, and 84 days.

The soil from each carton was transferrred to a 250-mL glass stoppered flask and shaken on a wrist-action shaker for 1 h with sufficient extraction solvent (acetonitrile:water:glacial acetic acid, 80:20:2.5 v/v/v) so that the total volume of extractant and water present in the soils was equivalent to 100 mL. After shaking, the soil was allowed to remain in contact with the extraction solvent for 20 h before being shaken for a further 1-h period. Soil extracts were then centrifuged at 2000 x g for 5 min and solvent-extractable radioactivity determined by radioassay of the supernatant (5mL).

A portion of the supernatant (25 mL) was added to 5% aqueous sodium chloride (100 mL) and extracted with dichloromethane (2 x 25 mL). The combined organic extracts were then evaporated to dryness under reduced pressure and the residue dissolved in methanol (25 mL), aliquots of which (5 mL) were examined for radioactivity. The remaining methanolic extracts were evaporated under reduced pressure to approximately 0.25 mL and examined using thin-layer chromatographic and radiochemical techniques for the presence of [14C]containing compounds.

Aqueous acidic acetonitrile, in conjunction with the extended extraction procedure, was used to recover the radioactive residues from the soils, since this method has proved most satisfactory for several aged residues of herbicides, including chlorsulfuron, from Saskatchewan field soils (Smith 1978, 1981; Smith and Hsiao 1985).

Precoated TLC plates (Silica Gel 60F-254, obtained from E. Merck, Darmstadt, Germany) were developed to a height of 10 cm above the origin and the air-dried chromatograms examined for radioactive compounds using a thin-layer chromatogram scanner. Non-radioactive standards run for comparative purposes were detected by viewing the developed chromatograms under a short-wave ultraviolet lamp. By comparing peak areas from the radio-chromatogram scans, and knowing the amounts of radioactivity extracted from each soil, the various radioactive products present were quantified. The Rf values of the compounds studied in three solvent systems are shown in Table 1.

Table 1. Rf values of compounds studied.

Compound	Rf I	 II	 III
Chlorsulfuron	0.74	0.45	0.41
2-Chlorobenzenesulfonamide	0.95	0.68	0.67
Metsulfuron methyl	0.29	0.37	0.31
2-Carboxymethylbenzenesulfonamide	0.95	0.66	0.62

I Acetonitrile; II Ethyl acetate:toluene:glacial acetic acid (50:50:1); III Acetone:hexane (1:1).

The radioactivity in the various solutions was measured by adding aliquots to scintillation solution (15 mL) consisting of an equivolume mixture of toluene and 2-methoxymethanol containing 0.4% of PPO and 0.1% of POPOP. Samples were counted using a liquid scintillation spectrometer, with counting efficiences being determined using an external [226Ra]standard.

RESULTS AND DISCUSSION

Extraction of [14C]chlorsulfuron- and [14C]metsulfuron methyl-treated soils after 1 h and after 7 days of incubation, followed by thin-layer and radiochemical analysis (Tables 2 and 3), confirmed that in both cases [14C] was being quantitatively recovered from the various soils, and that the parent herbicides were the main [14C]compounds present. It was also noted that the variation between each duplicate analysis never exceeded 5%.

Table 2. Radioactivity recovered from soils treated with 0.47 ug/g [14C]metsulfuron methyl following incubation at 20°C and 85% FC.

	% of applied [14C] extracted as					
	Sandy loam			Clay loam		
Time	Solvent ext.	M M	CMBS	Solvent ext.	M M	CMBS
1 h	100	100	<1	98	98	<1
7 d	100	98	2	95	86	9
14 d	95	95	<1	88	84	4
28 d	83	82	1	88	70	18
56 d	69	66	3	80	56	24
84 d	60	58	2	77	45	32

M M Metsulfuron methyl; CMBS 2-Carboxymethylbenzenesulfonamide.
Average from two replicates, variation less than 5%.

Table 3. Radioactivity recovered from clay treated with 0.47 ug/g [14C]chlorsulfuron and [14C]metsulfuron methyl following incubation at 20°C and 85% of FC.

	% of applied [14C] extracted as					
	Chlorsulfuron			Metsulfuron methyl		
Time	Solvent ext.	CS	CBS	Solvent ext.	M M	CMBS
1 h	100	100	<1	100	100	<1
7 d	100	100	<1	100	100	<1
14 d	97	97	<1	95	95	<1
28 d	98	92	6	92	90	2
49 d	93	83	10	84	83	1
70 d	92	76	16	78	76	2
98 d	86	67	19	72	69	3

CS Chlorsulfuron; CBS 2-Chlorobenzenesulfonamide; M M Metsulfuron methyl; CMBS 2-Carboxymethylbenzenesulfonamide.
Average from two replicates, variation less than 5%.

There was a steady loss of [14C]metsulfuron methyl with time in all soils (Tables 2 and 3), and this loss appeared to closely follow first-order kinetics, with the logarithm (base 10) of the percentage herbicide remaining being proportional to incubation time. By using regression analysis on the data from Tables 2 and 3, the half-life values for metsulfuron methyl in the clay loam, sandy loam and clay were 70, 102 and 178 days, respectively (Table 4). In addition to the parent herbicide, there was a second radioactively labeled compound present in all soils. This secondary compound had chromatographic properties identical to those for 2-carboxymethylbenzenesulfonamide (cf Table 1). This sulfonamide has been noted (Fisher 1984, personal communication) as a soil transformation product of metsulfuron methyl.

Table 4. Equations and half-life values for the degradation of chlorsulfuron and metsulfuron methyl in prairie soils.

Herbicide	Soil	Log_{10}(% herbicide) at T days	RMS	T1/2 days
Chlorsulfuron	Clay	2.0097 - 0.0018T	0.99	168
Metsulfuron methyl	Clay	2.0036 - 0.0017T	0.99	178
	Sandy loam	2.0062 - 0.0030T	0.99	102
	Clay loam	1.9759 - 0.0040T	0.98	70

RMS Regression mean square. T1/2 Half-life .

Amounts of the carboxymethylsulfonamide present in the soil varied according to type, but never accounted for more than 3% of the applied radioactivity in the clay and sandy loam (Tables 2 and 3). In contrast, in the clay loam where the breakdown was more pronounced, 32% of the initial metsulfuron methyl was in the form of the sulfonamide after 84 days (Table 2). No trace of any other compound was observed in any of the soil extracts. Furthermore at all sampling times and with all soils, more than 95% of the solvent extractable radioactivity was partitioned into the dichloromethane so that negligible amounts of [14C]products remained in the aqueous phase.

The results of the soil persistence studies with metsulfuron methyl (Tables 2, 3 and 4) indicate a tendency for the half-life to increase with increasing soil pH as has been reported for chlorsulfuron (Thirunarayanan et al. 1985). Thus, the half-life of metsulfuron methyl in the clay (pH 7.5) is more than twice that in the clay loam (pH 5.2).

[14C]Chlorsulfuron, like metsulfuron methyl, was degraded in the clay by an apparant first-order mechanism (Tables 3 and 4). The half-life of 168 days for chlorsulfuron was similar to that for metsulfuron methyl in the clay (Table 4). The known soil degradation product 2-chlorobenzenesulfonamide (Smith and Hsiao 1985) was also recovered from the clay treated with [14C]chlorsulfuron, and accounted for approximately 20% of the applied radioactivity after 98 days (Table 3). Only 3% of the applied [14C]metsulfuron methyl was in the form of the carboxymethylsulfonamide after the same period (Table 3); hence, it can be assumed that the chlorobenzenesulfonamide is more stable in the clay than is the carboxy-methyl analogue.

The half-life for chlorsulfuron in the clay was considerably greater than that of approximately 30 days reported (Walker and Brown 1983) for a moist sandy loam, with a pH of 7.1, at 20°C. However, results of other studies conducted in four soils under laboratory conditions at 75% of field capacity and at 20°C indicated (Thirunarayanan et al. 1985) that the rate of chlorsulfuron breakdown was dependent upon soil pH. Half-life values for chlorsulfuron were 89, 105, 137 and 143 days, in soils with pH values of 6.2, 7.1, 7.7 and 8.1, respectively (Thirunarayanan et al. 1985). These data indicate (Thirunarayanan et al. 1985) that at similar temperature and moisture conditions, the persistence of chlorsulfuron at soil pH 7.1 was almost three times greater in a clay loam than in a sandy loam (Walker and Brown 1983). In the present study, the half-life for chlorsulfuron (Table 4) in the clay (pH 7.5) was similar to the values noted by Thirunarayanan et al. (1985).

Since both chlorsulfuron and metsulfuron methyl have pKa values of about 3.7, they would be expected to exist as the highly water soluble dissociated species in most soil solutions. For this reason, adsorption of chlorsulfuron is pH dependent, and therefore very low on alkaline soils, but increases slightly as the soil pH increases (Mersie and Foy 1985; Thirunarayanan et al. 1985). These properties could also result in the greater leaching of chlorsulfuron and metsulfuron methyl in alkaline soils.

In the present experiments, as with those of other researchers (Thirunarayanan et al. 1985; Walker and Brown 1983), the laboratory persistence was evaluated in containers where leaching was restricted. For this reason the persistence of chlorsulfuron measured in the top 10 cm soil depths of small field plots in Saskatchewan 1 year after treatment may not give a true indication of the overall field persistence (Smith and Hsiao 1985). Both chlorsulfuron and the closely related herbicide sulfometuron methyl can undergo extensive leaching under field conditions (Nilsson 1984; Anderson and Dulka 1985). Thus in the field study (Smith and Hsiao 1985), where a carry-over of between 3 and 16% was noted in clay and sandy loam plots 1 year after treatment, leaching from the top soil could have occurred.

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