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Residual Fate of Metribuzin on Carrot (*Daucus carota*) Crop

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Metribuzin [4-amino-6-(1,1-dimethyl ethyl)-3-(methylthio)-1,2,4-triazin-5[4H]-one), is an asymetric triazinone herbicide used as a selective pre- and post-emergence herbicide. It has shown effective control of a large number of grassy and broadleaf weeds infesting agricultural crops such as soybean, sugarcane, corn, wheat and vegetables including tomato, potato and carrot (Worthing and Walker 1987).Residues of metribuzin were first analyzed and reported by Von Stryk (1971), using flame photometric detection in the sulfur mode. Webster et al. (1975) reported an electron capture gas chromatographic method for metribuzin and its metabolites using 5% OV- 225 on Chromosorb W. Later, Thornton and Stanley (1977) reported separation of metribuzin and its three metabolites in crops and soil using these GC conditions. Jarezyk (1983) simplified the extraction and cleanup procedure for micro estimation of metribuzin in soil and plant material.

This study describes the residues of metribuzin as estimated in carrot and carrot leaves from the point of view of safety to consumers and in soil from the point of view of safety to rotational crops.

MATERIALS AND METHODS

A field experiment was conducted in the farm of Division of Agronomy at IARI, New Delhi in rabi 1996. Carrot (*Daucus carota*) was raised according to the recommended package of practices in rabi 1996. Metribuzin (70% WP) was applied at the rates 300 and 400g a.i. ha^{-1} both as pre- and post-emergent spray. The treatments were quadruplicated in randomized block design. IARI alluvial soil, a sandy loam has texture with a composition of 19% clay, 21% silt, 60% sand and 0.35% organic carbon and a pH of 7.2.

Soil samples from two doses (300 and 400g a.i./ha) of pre-emergent treatment on 0 (4 h), 14, 24 and 84 days (harvest time) from 0-5 and 5-10 cm depths were collected using a tube auger from each replicate. Carrot fruits and leaves samples were also drawn from these two pre-emergence applications at harvest from all the replicates.

A representative soil sample (100 g) was extracted with 200 ml of methanol :

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supernatents in the separating funnel and extracted with dichloromethane (200 + 100 + 100 ml). The organic layer was separated and dried over anhydrous sodium sulphate (10 g) through a fluted filter paper. The solvent was evaporated to dryness on a rotary evaporator. The remaining aqueous phase was discarded. Residues were dissolved in hexane : acetone (4:1) prior to injection into GLC. Chopped leaves and carrot samples (100 g) were separately blended with acetonitrile (200 ml) for about 2 minutes in the Waring blender. The macerates were filtered through a suction filter. The filtered cake was reblended with 200 ml of acetonitrile and filtered. Finally it was washed with acetonitrile (50 ml). The filterates were combined in a round bottomed flask (500 ml) and rotary evaporated until solution was free of acetonitrile. The leftover aqueous residue was chilled in an ice bath. The precipitated contents were filtered immediately. Filtrate was taken in a separating funnel (500 ml), water (100 ml) was added and contents were extracted with dichloromethane (200 + 100 ml). The organic layer was passed over anhydrous sodium sulphate through a fluted filter paper into a round bottomed flask and rotary evaporated to dryness. For further cleanup, residues in hexane were transferred to a glass column (20 cm x 2 cm i.d.) packed with 10 cm of Florisil overlayed with anhydrous sodium sulphate (1cm) and eluted first with hexane (100 ml) followed by methanol (100 ml). The dried methanol fraction containing metribuzin was evaporated on rotary evaporator to dryness and volume made up in hexane : acetone (4:1) prior injection in GC.

Residues were estimated on a gas chromatograph (HP 5890 A) using Ni^{63} electron capture detector. Aliquots (3 µl) of extracts were injected into megabore column (20µm film thickness) packed with HP-17 at a column, injector and detector temperatures of 185, 250 and 275°C respectively. The flow of carrier N_2 gas was 25 ml min^{-1}. Under these conditions metribuzin gave a sharp peak at a retention time (R_t) of 3.54 min.

Recovery experiments were run on carrot, leaves and soil by spiking with known quantity of metribuzin before the initial extraction and analysing the residues by the method described above. Recoveries of metribuzin were in the range of 75-82% at levels of 0.1 and 0.5 ppm.

RESULTS AND DISCUSSION

Metribuzin soil dissipation studies conducted under field conditions, revealed that initial residues of 0.303 and 0.479 ppm were reduced to 0.074 and 0.128 in 0-5cm soil depth in about 84 days from normal and higher dose of herbicide application (Table 1). There was evidence of movement of metribuzin to lower depth (5-10 cm) within 14 days and that it persisted till harvest. It was observed that metribuzin dissipated in field soil to approximately 34 percent in 14 days, 40 percent in 24 days and 74 percent in 84 days (harvest time) irrespective of rate of its application. Like other herbicides of triazine group, metribuzin showed sufficient persistence with half-life of 61 days in soil under field conditions.

Table 1. Metribuzin residues* (ppm) in soil after pre-emergence application

Days after application	Soil Depth (cm)	Metribuzin application rate (g a.i./ha)			
		300		400	
		Residues ±S.D.	Dissipation (%)	Residues ±S.D.	Dissipation (%)
0	0-5	0.303 ± 0.032	--	0.479±0.050	--
14	0-5	0.215 ± 0.080	29.04	0.297±0.004	37.99
	0-10	0.082 ± 0.005		0.104±0.012	
24	0-5	0.189 ± 0.005	37.60	0.269±0.070	43.84
	5-10	0.063 ± 0.070		0.088±0.005	
84	0-5	0.074 ± 0.010	75.57	0.128±0.020	73.28
	5-10	0.049 ± 0.025		0.053±0.015	
Rate Constant 'K'		0.0113		0.0114	
Correlation 'r' Coefficient		-0.990		-0.999	
Regression Equation		y = 0.512 – 0.0049x		y = 0.689 – 0.0050x	
RL (50) 'days'		61		60.78	

*Mean of three replicates

Metribuzin residues were determined in leaves and carrots at harvest from both the dosage after pre- and post- emergence application. Persistence and translocation of metribuzin to leaves and carrots was evident from the residue detected at harvest (Table 2). Residues of 0.021 and 0.063 ppm were detected in carrots from pre - emergence application at normal and higher rates of metribuzin. Post-emergence application of metribuzin in carrot produced phyto-toxicity to the crop plants to the extent that leaves were totally damaged and were not available for residue estimation. Carrots produced were deformed and much smaller in size compared to those produced from pre-emergent application of metribuzin. Metribuzin residues of 0.160 and 0.370 ppm in carrots. From normal and higher dosages of post emergence application were not within safe limits of 0.1 ppm of metribuzin for carrots.

Table 2. Harvest time residues of Metribuzin in leaves and carrots

Application	Dose (g a.i./ha)	Residues (μg/g)*	
		Leaves	Carrot
Pre-emergence	300	0.059	0.021
	400	0.102	0.063
Post-emergence	300	Leaves damaged	0.160
	400	Leaves damaged	0.370

* Average of three replicates

Metribuzin was found to sufficiently persist when applied as pre-emergence at rates as low as 300 g a.i./ha. About 25% residues persisted in sandy loam field soil under Indian tropical conditions. The half-life in soil was 2 months irrespective of the rate of application. Residues, though less than 0.1 ppm, were detected in carrots at harvest and were safe for consumption considering MRL of 0.2 ppm for this vegetable. Post-emergence application of metribuzin in carrots produced phytotoxicity to crop and carrots. Detected high level of metribuzin residues were also unsafe for human consumption.

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