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Metribuzin dissipation pattern in soil and its residue in soil and chilli

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ABSTRACT

Field study was carried out to determine the dissipation of metribuzin and its residues in soil and chilli. Vermicompost (2 t/ha) was used as organic amendments to enhance the degradation. Metribuzin was applied at single and double the dose of 500 and 1000 g/ha. The chilli variety '*Krishna Jolokia*' was grown with a recommended practices. The recoveries obtained for untreated soil and chilli were in acceptable range of (80.6–85.7%) and (86.8–92.2%) of the metribuzin standards and spiked samples. The limit of detection (LOD) – 0.003 µg/g and the limit of quantification (LOQ) – 0.01µg/g in soil and chilli. The metribuzin residue level ranged 0.153 – 0.356 µg/g on the day of application of metribuzin and further degraded to 0.023 – 0.087 µg/g on the 21st day of application. However, the half-life of metribuzin was observed to be 7 and 10 days with single and double the dose of application of metribuzin. Metribuzin residues did not persisted in soil beyond 30 days after application and in fruits.

Assam is known worldwide for the genetic diversity and hotness of the varieties of chillies. Crop weed competition for the space, water and nutrient at the early stage of growth period is not desirable as it affects the crop growth, yield and the nutritional quality. At present, weed management through herbicides has become more popular as compared to manual weeding in view of labour shortage and higher cost involvement. Metribuzin (4-amino-6-tert-butyl-3-methylthio-1, 2, 4- triazine- 5- one), a triazine herbicide is photo system II inhibitor.It binds to a protein of the photosystem II complexthat disrupts the electron transport chain. It has been observed that foliar applied metribuzin is moderately absorbed into the plant. Metribuzin can be used as a pre and post-emergence herbicide. As pre-emergence herbicide, metribuzin efficacy is based on the presence of soil moisture for broad spectrum weed control. It is commonly used for management of broad-leaf and grassy weeds in vegetables like crops like potato, chilli and tomato *etc*. The availability of metribuzin for plant absorption is affected mostly by soil pH (James *et al*. 1976). Herbicides vary in their potential to persist in soil. Herbicides that can persist to the next season may injure succeeding crops and require close monitoring. Metribuzin persistence in the soil does not significantly affected by the straw mulch present on the soil surface (Philip and Edward 2017). Differences occur in the sensitivity and tolerance of crop varieties against herbicides, which are consequently significant for practical crop protection. Due to the soil properties like large surface area and porosity, metribuzin adsorption is more prominent in soil (Oren and Chefetz 2012). Soil physico - chemical properties have significant effect on metribuzin adsorption capacity in soil and plant system (Ara *et al*. 2013) .Hence the present study was conducted to know the residue accumulation and dissipation of metribuzin in fruit and soil of chilli.

A field trial was conducted at Instructional cum Research Farm, Assam Agricultural University, Jorhat during 2016-17. The Chilli variety "*Krishna Jolokia*" was grown in plots with 4 x 3 m in size with a spacing of 45 x 45 cm and was arranged in a randomized block design with four replications. The treatments comprised of metribuzin 500 g/ha, and metribuzin 2 x 500 g/ha as pre-emergence. The physico - chemical parameters of the soil was determined by following the procedures suggested by Piper, 1966; Jackson, 1973 and Subbiah and Asija, 1956. The soils of the experimental field was acidic (pH-4.8), sandy clay loam in texture and had CEC - 8.46 c mol (p^+)/kg, organic carbon - 0.68% , available N - 264.74, P_2O_5–20.68, K_2O–76.98 kg/ha, respectively. The climatic conditions of Jorhat, as a whole, were sub-tropical and humid having summer and cold winter. Normally, monsoon rain starts from the month of May - June and continues up to the month of September-October. The meteorological parameters have been

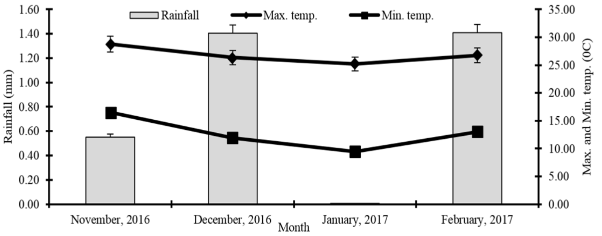

Figure 1. Maximum, minimum temperature, rainfall during metribuzin dissipation period in soil

presented in **Figure 1**. The recommended dose of fertilizer was120:60:60Kg/ha of N, P_2O_5 and K_2O respectively. The full doses of N,P and K and organic sources (vermincompost at 2 t/ha) was applied as basal.

Chemicals and reagents: Metribuzin was supplied by the company Sigma-Aldrich. Chloroform AR grade (e" 99.9%), methanol, dichloromethane and n – hexane were purchased from Merck Pvt. Ltd., Mumbai.

Preparation of the standard solutions: A stock solution of 1000 µg/g metribuzin was prepared by dissolving 100 mg of technical grade herbicide in 100 ml hexane. Further dilutions were made to make 100,10 and 1 µg/ ml hexane solution and internal standard solutions were stored at – 20^0 C in deep freeze until use. The reference standard of metribuzin was used for quantification, recovery and determination of retention time of metribuzin.

Sample collection and preparation: Representative composite surface soil (0-15 cm) and chilli samples were collected where no herbicides were applied for fortification study by feeding with known concentration of the metribuzin standards. Similarly, soil samples were collected periodically at 0,3,7,15,21 and 30 days from the day of metribuzin application (within 4 hours of herbicide application) as well as to thirty days after application. A part of soil and plant samples were collected after harvest of the chilli crop. Control as well as blank samples were maintained to check for the contamination and interferences. The soil samples were processed and stored in polythene bags for analysis of various physico–chemical parameters and herbicide residue by following standard protocols which directly or indirectly affects the factors like degradation, dissipation, adsorption and leaching of the metribuzin applied to field. The representative fruit (20 g) and soil (20 g) sample were weighed and blended separately and the samples were transferred to a shaking bottle and shaken on over end shaker after adding 60 ml of methanol: water 1:1 (v / v) for30 minutes. The resulting slurry was filtered through filter paper; the bottle was washed with additional 50 ml of methanol: water and the washings were filtered and left for 5 min.

Clean up and estimation: Partitioning and column clean-up was performed by transferring the combined extract and washing to separatory funnel. Methanol extract was partitioned with dichloromethane three times sequentially (3 x 20 mL) in presence of 30 ml of 2% aqueous sodium sulphate solution. The combined dichloromethane extracts were evaporated to dryness by using rotary evaporator, dissolved with 10 ml petroleum ether and subjected to chromatographic column determination. The column was pre washed with 4 ml petroleum ether: acetic ether 98:2 (v / v) which was discarded. Analytes were eluted with 5 ml petroleum ether: acetic ether 90: 10 (v / v). The eluate was evaporated to dryness in the rotary evaporator and the residues were re dissolved in 5 mln – hexane.

Instrument and operating conditions: The metribuzin residues were estimated by injecting samples to the Gas Chromatography with model No. GC–1000 and Series No. 2015/0505 having mega pore capillary column, 30 M, length x 0.25 mm, I.D. x 0.25micro metre, film thickness, Column – TG – 5MS GC column, Carrier gas – Nitrogen (> 99.999%), Flow rate – 40 mL/min, Detector – Electron Capture Detector (ECD) , Oven temperature - 210 ^{O}C injector Temperature - 240 ^{0}C – Detector temperature – 260 ^{0}C, Retention time - 3.09 min.

Injection volume : 0.5 µL

Determination of recovery: Recovery experiment was done for validation of the method described for the sample preparation. Untreated soil and fruit samples were fortified with known amounts of working standard solutions (0.01, 0.05, 0.1, 0.5 µg/ g) and processed according to the above procedures .Every recovery was done on five replications.

Method validation: Calibration curve for metribuzin was prepared by injecting different known concentrations (0.01, 0.05, 0.1, 0.5 and 1 µg/g) of the compound. A calibration curve have been plotted for the concentrations of the standards injected versus the peak area observed and the curve area was found to be linear up to the lowest concentration range of 0.01 µg/g.The approximate retention time was obtained at 3.1 minutes.

The regression equation and correlation coefficient (R^2) for metribuzin standard was as follows.

$$Y = 3255.07904 X + 296.42591. \quad R^2 - 0.98\ 99$$

The recoveries obtained for untreated soil and chilli were in acceptable range of (80.6 – 85.7%) and (86.8–92.2%) (**Table 1**) of the metribuzin standards and spiked samples.

Precision and detection and quantification limits: The limit of detection (LOD) – 0.003 µg/g in fortified soil and chilli. Based on signal to noise ratio **t**he limit of quantification (LOQ) for the method was defined as the lowest concentration of the compound in a sample

Table 1. Per cent recovery of metribuzin from fortified samples of soil and chilli

Sample spiked (mg/kg)	Percent recovery	
	Soil	Fruit
0.5	85.7	92.2
0.1	83.1	90.0
0.05	82.4	88.6
0.01	80.6	86.8
Mean	83.0	89.4

that could be quantitatively determined with suitable precision and accuracy. The limit of quantification (LOQ) – 0.01µg/g in fortified soil and chilli.

Degradation of metribuzin and residue dissipation: The decrease in residue levels during the days after application in soil is presented in **Figure 2**. The metribuzin residue level ranged 0.153–0.356 µg/g on the days after application (DAA) of metribuzin and observed up to the ranged 0.023 – 0.087 µg/g on the 21st DAA of metribuzin. The metribuzin residue level was observed at below detection limit (BDL) from 30th DAA of metribuzin. The dissipation of metribuzin in soil followed a pseudo first order kinetics (Khoury *et al*. 2006).The metribuzin degradation and dissipation is strongly dependent on temperature (Benoit *et al*. 2007). Application of organic manure significantly increased the retention of metribuzin in soil (Mazumdar and Singh 2007). Khoury *et al*. (2006) stated that soil microbes has important role in the rapid degradation of metribuzin in soil. Intense leaching was due to low adsorption of metribuzin in soil (Lagat *et al*. 2011).

The half life ($T_{1/2}$) and dissociation coefficient (k) calculated for single and double dose of applications were presented in **Table 2**, with a half-life of 7–10 days and dissociation coefficient of 0.07-0.09/days. The half-life of metribuzin is dependent on factors like soil moisture content, pH, temperature and depth of application (Smith and Walker 1989). Metribuzin in field soil have shorter half-life over that of sterile soil (Ivany *et al*. 1983) due to the presence of native microbial population in soil.

Table 2. Half life and dissociation coefficient

Rate of application	X (500 g/ha)	2X (1000 g/ha)
Half Life (T1/2) days	7.43 ± 0.23	10.33 ± 0.17
Dissociation coefficient (k)/days	0.093 ± 0.003	0.067 ± 0.005

Recovery investigation for validation of method used for sample preparation resulted acceptable range of (80.6-92.16%) for the substrates with the retention time of 3.097 minutes. The goodness of fit was 0.9899 for calibrating the standard curve of metribuzin, From the present investigation it can be concluded that there was no persistence of metribuzin residue in soil beyond 30 DAA and in fruits at harvest with a half life of 7–10 days. Therefore, the organic manure in soil is to be well incorporated to minimize the residue build up in soil.

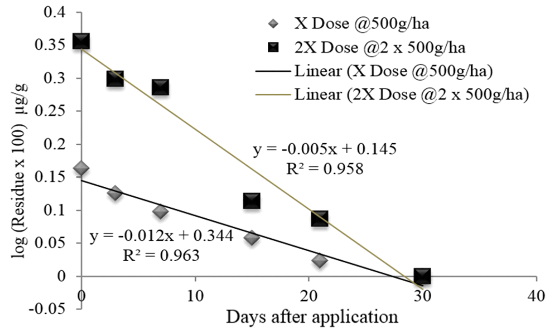

Figure 2. Dissipation of metribuzin in soil

REFERENCES

Ara B, Shah J, Jan MR, Aslan S. 2013. Removal of metribuzin herbicide from aquous solution using corn cob. – *International Journal of Science, Environment and Technology* **2**(2): 146–161.

Benoit P, Perceval J, Stenrod M, Moni C, Eklo OM, Barriuso E, Sveistrup T and Kvaemer J. 2017. Availability and biodegradation of metribuzin in alluvial soils as affected by temperature and soil properties .*Weed Research* **47(6)**: 517–526.

Ivany JA, Sadler JM and Kimball ER, 1983. Rate of metribuzin break down and residue effects on rotation crops. *Canadian Journal of Plant Science* **63**: 481–487.

Jackson, ML. 1973. *Soil Chemical Analysis.* Prentice Hall of India Pvt. Ltd.

James S, Ladlie, William F, Meggitt and Donald P. 1976. Effect of pH on metribuzin activity in the soil,*Weed Science* **24**(5): 505–507.

Khoury R, Coste CM and Kawar NS. 2006. Degradation of metribuzin in two soil types of Lebanon. *Journal of Environmental Science Health*, Part B: *Pesticides, Food Contaminants and Agricultural Wastes* **41**: 795–806.

Lagat SC, Lalah JO, Kowenje CO and Getenga ZM. 2011Metribuzine mobility in soil column as affected by environmental and physic chemical parameters in Mumias sugarcane zone,Kenya,ARPN *Journal of Agricultural and Biological Science* **6**(B): 27–33.

Majumdar K and Singh N. 2007. Effects of soil amendments on sorption and mobility of metribuzine in soils. *Chemosphere* **66**(4): 630–637.

Oren A, Cheftz B.2012 Successful sorption and desorption cycles of dissolved organic matter in mineral soil matrices. *Geoderma,* 189–190; 108–115 .

Philip A, Banks and Edward L. Robinson. 2017. The influence of straw mulch on the soil reception and persistence of metribuzine. *Weed Science* **30**(2): 164–168.

Piper CS. 1966. *Soil and Plant Analysis*. Hans Publisher, Bombay, India, pp. 368–370.

Smith AE and Walker A. 1989. Prediction of the persistence of the triazine herbicide-atrazine, cyanazine and metribuzine in Regina heavy clay. *Canadian Journal of Soil Science*, **69**(3): 587–595.

Subbiah BV and Asija GL. 1956. A rapid procedure for the determination of available nitrogen in soil. C*urrent Science* **25**: 256–260.