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Persistence of Metribuzin in Tomato Growing Soils and Tomato Fruits

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ABSTRACT

Dissipation of metribuzin and its persistence in tomato fruits was studied by conducting on-farm research trials in three farmer's fields in Ranga Reddy district of Telangana state. Farmer's fields with widely varying soil characteristics were selected and metribuzin was applied at 500 g a.i. ha^{-1}. Soil samples were collected at 0, 7, 15, 30, 45 and 60 DAA (days after application) and fruit samples were collected at harvest and analysed on GC-ECD for metribuzin residues. Metribuzin persisted in the soils up to 45 DAA in coarse textured soils and 60 DAA in medium and fine textured soils. Metribuzin leached to 20-30 cm depth in all the soils and leaching was more pronounced in coarse textured soils than in fine textured soils. Organic carbon and clay content significantly influenced the residual life and leaching of metribuzin in soil. In soils, metribuzin dissipation followed a first-order decay process and exponential model was found to give better fit for field dissipation. Half life of metribuzin soil varied from 9.11 to 21.15 days. Metribuzin residues in tomato samples collected at the time of harvest were below the detection limit and MRL of 0.05 mg kg^{-1} in all the farmer's fields.

INTRODUCTION

Application of herbicides for control of weeds has become an integral and indispensable part of modern day agriculture. Metribuzin is a selective post emergence herbicide used in tomato for broad-spectrum control of weeds. In Ranga Reddy district of Telangana State, metribuzin is the most popular post-emergence herbicide used by tomato growers.

The fate of soil applied herbicide depends on its adsorption, desorption and leaching in the soil. Herbicides belonging to the triazine family are adsorbed onto clay minerals through hydrophobic interactions with the siloxane surface. These interactions are favourable in swelling minerals when the interlayer space is saturated with common soil elements such as K, whereas adsorbed Ca and Mg decrease herbicide-clay interactions. This is due to the lower hydration of the cation to which the herbicide is complexed or to the higher partial dehydration of the herbicide molecules therefore increasing the contacts of the herbicide in the interlayer space with the two clay layers. Nevertheless, these herbicides are readily adsorbed on montmorillonite saturated with Ca (Agarwal et al. 2006). Sorption capacity of soil increases with increasing organic carbon content of the soil. Significant correlation in linear regression analysis between adsorption capacity and soil organic carbon content was observed (Prakash et al. 2000). Metribuzin has a lower affinity than atrazine or metolachlor for clay loam soil and it has readily translocated to deeper layers with rain (Gaynor et al. 2000)

Information on the persistence and leaching potential of metribuzin in soils is of practical importance, especially in determining the rotation restrictions for succeeding susceptible crops and groundwater contamination potential of the herbicide respectively. Information on the persistence and leachability of metribuzin in soils with different physical, physico-chemical properties and its persistence in tomato fruit under farmer's field situations is lacking. Hence, the present experiment was conducted.

MATERIALS AND METHODS

Collection of Soil and Tomato Fruit Samples

Three tomato growing farmers were selected for conducting the on-farm experiment and collection of the soil and fruit samples in Chenvelly village Ranga Reddy district of Telangana state during *rabi* season. All the farmers applied the recommended dose of metribuzin @ 500 g a.i. ha^{-1} as post emergence spray at 15-20 DAT (days after transplanting). In this experiment, depth wise (0-10 cm, 10-20 cm and 20-30 cm) soil samples and fruit samples were collected from farmer's fields. Soil sampling was done at 0 (2 hours after the application of herbicide), 7, 15, 30, 45, 60 days after application of the herbicide and at first harvest. Tomato fruit samples were collected at the first, second and third harvests. Soil samples were collected from different spots in the selected field to obtain a composite sample. The representative sample (500 g) was collected from the composite sample by following standard quartering method.

Table 1: Initial values of the collected soil samples.

Sample	pH	EC (dSm^{-1})	OC (%)	Clay content(%)	Texture
Farmer-1	7.12	0.056	0.53	21.12	Sandy clay loam
Farmer-2	8.06	0.124	0.49	33.46	Clay loam
Farmer-3	6.74	0.065	0.32	13.46	Sandy loam

The collected soil samples were brought to the laboratory, air dried in shade, passed through a 2.0 mm sieve, labelled and stored in polythene bag stored in a -20°C freezer. Tomato fruit samples were collected from a farmer's field, from where the soil samples were collected. The collected samples were stored in -20°C freezer for analysis.

Analysis of the soil samples for physical and physico-chemical properties: Analysis of soil samples for pH, EC, organic carbon and texture were done employing standard procedures. The physical and physico-chemical properties of these three collected soil samples from farmer's fields are presented in Table 1. The pH of these samples was in the range of 6.74 to 8.06 (slightly acidic to moderately alkaline). Electrical conductivity varied from 0.056 to 0.124 dS m^{-1}. Organic carbon of these samples were low to medium. Farmer's sample 3 had low organic carbon (0.32 %) whereas farmer's sample 1 having medium organic carbon (0.53 %). Texture of the experimental sites was sandy loam to clay loam. Farmer's sample 2 was classified as clay loam texture with clay content of 33.46 %. Very low clay content (13.46 %) was recorded in farmer's sample 3 and texture was sandy loam. Farmer's sample 1 was sandy clay loam in texture with 21.12% clay content.

Metribuzin Estimation in Soil and Tomato Samples

Metribuzin residues in the soil samples were extracted using the procedure outlined by Bedmar et al. (2004). In the tomato fruit samples, metribuzin residues were assessed using the procedure as described by Kirchhoff (1994).

Soil Samples

Soil samples were extracted with 50 mL mixture of acteonitrile and water (1:5 ratio) in a horizontal mechanical shaker for one hour, filtered and partitioned with dichloromethane (50 mL). The soil samples were filtered through anhydrous sodium sulphate for dehydration and concentrated to 2.0 mL on a water bath. This residue was transferred to a silica gel column for cleanup and it was eluted with 50 mL of dichloromethane. The collected elute was concentrated on a water-bath to 10 mL and analysed on GC for residues.

Tomato Samples

Tomato fruit samples (100 g) were blended in a homogenizer and 200 mL acteonitrile. Filtration of the homogenate was done with suction through a glass filter funnel. The process was repeated with 200 mL acetonitrile. This entire acteonitrile residue mixture was evaporated on a rotary-vacuum evaporator until free of acetonitrile. Combined filtrates were extracted with 200 and 100 mL portions of dichloromethane. Combined dichloromethane phases were filtered through 10 g sodium sulphate evaporated to dryness in rotary vacuum evaporator. The residue was dissolved in methanol and injected into GC-ECD for estimation of metribuzin residues.

GC Parameters

Metribuzin residues were estimated in Shimadzu GC 2010 (ECD with Ni^{63}) with capillary column AB-5 of 30 m length, ID (internal diameter) of 0.53 mm, film thickness 1.50 micrometer. Nitrogen was used as the carrier gas at a flow rate 3.50 mL/min. Column, injector and detector temperatures were set at 230°C, 210°C and 250°C, respectively.

RESULTS AND DISCUSSION

Persistence of Metribuzin in Soils

Persistence of metribuzin in the soils at different days after application is presented in Table 2. Metribuzin persisted in the soils up to 60 DAA in the soil samples drawn from farmers 1 and 2. Whereas, in case of farmer 3, residues could be detected up to 45 DAA, beyond which the residues were below the detection limit of 0.05 mg kg^{-1}.

Initial concentration of metribuzin in the surface samples (0-10 cm) (on 0 days, 2 hours after application of the herbicide) in the soils varied between 0.343 to 0.386 mg kg^{-1} and no residues of metribuzin could be detected in the 10-20 and 20-30 cm layer soil samples. At 15 DAA, highest metribuzin concentration in the 0-10 cm layer was reported in clay soil (farmer-2) and lowest was recorded in sandy loam soil (farmer-3). However, significant leaching of the applied herbicide into the deeper layers was observed in the coarse textured soils of farmer 3 (0.096 mg kg^{-1}), and the corresponding residue concentration in case of farmer 1 and farmer 2 were 0.079 and 0.056 mg kg^{-1} respectively. Metribuzin residues could be detected in the 20-30 cm layer also at 15 DAA in all the sampling locations. Distributions of metribuzin in different soil layers indicated the potential mobility of the applied metribuzin to the soils.

At 30 DAA, metribuzin concentration detected in the surface layer (0-10 cm) varied from 0.065 mg kg^{-1} (farmer 3) to 0.124 mg kg-1 (farmer 2). Metribuzin could not be detected in the 20-30 cm layer in the samples drawn from

Table 2: Persistence of metribuzin in soil samples.

Days after application	Metribuzin residues ($mg.kg^{-1}$)								
	Farmer-1			Farmer-2			Farmer-3		
	0-10cm	10-20cm	20-30 cm	0-10cm	10-20cm	20-30 cm	0-10cm	10-20cm	20-30 cm
0	0.386	BDL	BDL	0.343	BDL	BDL	0.375	BDL	BDL
7	0.256	0.062	BDL	0.214	0.050	BDL	0.197	0.128	BDL
15	0.146	0.079	0.052	0.156	0.056	0.052	0.104	0.096	0.075
30	0.102	0.055	BDL	0.124	BDL	BDL	0.065	0.053	BDL
45	0.072	BDL	BDL	0.082	BDL	BDL	0.056	BDL	BDL
60	0.056	BDL	BDL	0.066	BDL	BDL	BDL	BDL	BDL
Harvest (85)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

farmers 1 and 2. This could be due to stronger sorption of the herbicide with the higher amount of the clay present in the soil of farmer 2. No leaching of residue could be observed into deeper layers at 45 DAA. Surface soil concentration of metribuzin varied from 0.056 to 0.082 mg kg^{-1}. Similar leaching of metribuzin was earlier reported by Harper (1988) and Locke & Harper (1991). The higher concentration of the metribuzin in deeper layers in case of the coarse textured soils (farmer 3) indicated the higher leaching potential in these soils due to lesser adsorption on clay, presence of low-active clays and lower organic carbon content compared to the other two soils. Lagat et al. (2011) and Gaynor et al. (2000) reported a higher leaching potential of metribuzin in coarse textured soils and soils with low organic carbon, respectively.

No metribuzin residues could be detected in soils of farmer 3 at 60 DAA. Whereas, the residues of the metribuzin could be detected in the other two soils at 60 DAA, beyond which they reached BDL. These findings corroborate with the results of earlier lab experiments conducted, which indicated stronger adsorption and higher hysteresis in soils with higher clay and organic matter content. Similar results were earlier reported by Selim (2004) for metribuzin and DWM (2012) in case of atrazine applied to sweet corn.

Dissipation trends of the metribuzin in soil: Initial detected amount (IDA) of herbicide in soil varied from 0.386 to 0.343 mg kg^{-1} in different farmer's fields on 0 DAA (2 hours after application). Dissipation of the herbicide in the soil is presented in Fig. 1. Different curves of fit were tested to predict the dissipation behaviour of the herbicide. Among the models tested (linear, polynomial, logarithmic and exponential) the exponential model was found to give a better fit for field dissipation of the metribuzin in soil. Mathematically, metribuzin dissipation followed a first-order (pseudo first-order) decay process:

$$C=C_o exp^{-kd.t} \quad ...(1)$$

Where, C_o is the initial concentration in soil, C is the concentration in the soil after t days, and K_d is the dissipation rate coefficient. The linearized equation 1 is:

$$\log (C/C_0) = -0.4343\ K_d\ t \quad ...(2)$$

Applying equation 2, dissipation trends of the propaquizafop at different doses of application was as follows.

Farmer-1 $y = 0.302e^{-0.03x}$ $R^2 = 0.93$ ...(3)

Farmer-2 $y = 0.278e^{-0.02x}$ $R^2 = 0.95$ ...(4)

Farmer-3 $y = 0.270e^{-0.04x}$ $R^2 = 0.87$ ...(5)

Using the above exponential equations (3 to 5) the half-life (DT_{50} time taken in days, for 50 % dissipation of the initial detected amount) was calculated. The field dissipation studies in different soils indicated that, the half-life (DT_{50}) of metribuzin varied from 9.11 to 21.15 days. In case of farmer 1, where the soil was medium in texture with medium organic carbon content, the DT_{50} was 14 days. The longest half-life metribuzin in soil was observed in soil of farmer 2 (21.15 days) and shortest half life of 9.11 days was noticed in farmer 3. These half-life reported for metribuzin are in agreement with the findings of Khoury et al. (2006).

There is a strong correlation between the metribuzin persistence in soil and clay content of the soil and organic carbon content. The higher clay content and organic carbon content were found to positively influence the persistence of the metribuzin in the soil. Similar results depicting prolonged persistence of metribuzin in soils with higher organic carbon content (Patrick, 1998) and higher clay content (Khoury et al. 2003) was earlier reported. This mechanism behind the enhanced persistence of metribuzin in fine textured soils appears to be similar with the results of Allen & Walker (1988), Johnson & Pepperman (1995), Moon (1996), and Hernandez et al. (1998). Even though, there is no universally accepted

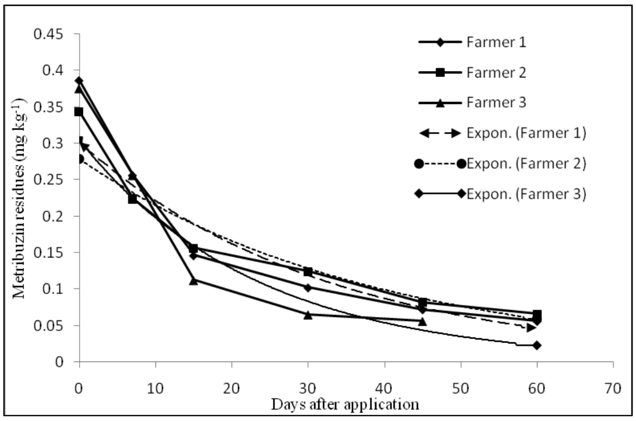

Fig. 1: Dissipation pattern of metribuzin in surface soils.

classification of pesticide environmental persistence, propaquizafop can be categorized as slightly persistent in the soil by using Roberts (1996) classification based on the mean half-life of the pesticide in the soil.

Metribuzin Tomato Fruit Samples

Metribuzin residues in tomato samples collected at the time of harvest were below the detection limit of 0.05 mg kg^{-1}. The MRL for metribuzin in tomato is 0.05 mg kg^{-1} (GAIN 2010). Similar results in case of potato were earlier reported by Hu et al. (2010).

CONCLUSION

Metribuzin residues persisted for a longer period of 60 DAA in the soil samples with higher organic carbon content and clay content due to higher sorption of metribuzin on clay and organic carbon. In coarse textured soil with low clay and organic carbon, the metribuzin residues could be detected up to 45 DAA. Half-life of metribuzin in soils varied from 9.11 to 21.15 days. At the time of harvest no residues of metribuzin could be detected (0.05 mg kg^{-1}) in tomato fruit and soil.

REFERENCES

Agarwal, V., Li, H. and Teppen, B.J. 2006. Triazine adsorption by saponite and beidellite clay minerals. Environmental Toxicology and Chemistry, 25: 392-399.

Allen, R. and Walker, A. 1988. The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. Pesticide Science, 18: 95-111.

Bedmar, F.M., Costa, J.L., Sciero, E. and Gimenez, D. 2004. Transport of atrazine and metribuzin in three soils of the humid pampas of Argentina. Weed Technology, 18: 1-8.

DWM 2012. Directorate of Weed Management Centre, Hyderabad, Annual Report. pp.71

GAIN (Global Agricultural Information Network) 2010. GAIN Report Number: CH10059, pp. 11

Gaynor, J. D., Tan, C.S., H.Y.F. Ng., Drury, C.F., Welacky, T.W. and Van Wesenbeeck 2000. Tillage and controlled drainage subirrigated management effects on soil persistence of atrazine, metolachlor, and metribuzin in corn. Journal of Environmental Quality, 29(3): 936-947.

Harper, S.S. 1988. Sorption of metribuzin in surface and subsurface soils of the Mississippi delta region. Weed Research, 38: 84-89.

Hernandez, F., Beltran, J., Forcada, M., Lopez, F. and Morell, I. 1998. Experimental approach for pesticide mobility studies in the unsaturated zone. International Journal of Environmental Analytical Chemistry, 71: 87-103.

Hu, J., Zhubo, Deng, Chang, Liu and Zhixin, Zheng 2010. Simultaneous analysis of herbicide metribuzin and quizalofop-p-ethyl residues in potato and soil by GC-ECD. Chromatographia, 72(7/8): 701-706.

Johnson, R.M. and Pepperman, A.B. 1995. Soil column mobility of metribuzin from alginate-encampsulated controlled release formulation. Journal of Agricultural Food Chemistry, 43: 241-246.

Khoury, R., Coste, C. M. and Kawar, N. S. 2006. Degradation of metribuzin in two soil types of Lebanon. Journal of Environmental Science and Health, Part B, 41: 795-806.

Khoury, R., Geahchan, A., Custe, C.M., Cooper, J.F. and Bobe, A. 2003. Retention and degradation of metribuzin in sandy loam and clay soils of Lebanon. Weed Research, 43: 252-259.

Kirchhoff, J. 1994. Manual of Pesticide Residue Analysis, Pesticide Commission.

Lagat, S.C., Lalah, J.O., Kowenje, C.O. and Getenga, Z.M. 2011. Metribuzin mobility in soil column as affected by environmental and physico-chemical parameters in Mumias sugarcane zone, Kenya. ARPN Journal of Agricultural and Biological Science, 6(3).

Moon, Y.H. 1996. Evaluation of three pesticide leaching models with experimental data for alachlor, atrazine and metribuzin. Weed Research, 36: 37-47.

Patrick, S. 1989. Role of humic organic matter in herbicide adsorption. Weed Technology, 3(1): 190-197.

Prakash, N.B., Suseela Devi and Siddaramappa, R. 2000. Effect of organic amendments on persistence of butachlor and pendimethalin in soils. Pesticide Research Journal, 10(2): 202-208.

Roberts, T.R. 1996. Assessing the fate of agrochemicals. Journal of Environmental Science and Health, 31(3): 325-335.

Selim, H.M. 2004. Modeling kinetic retention of atrazine and metribazin in soils. Soil Science, 169: 29-34.