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Leaching potential of metribuzin in agricultural soils

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Abstract
Metribuzin is a triazinone herbicide used as a pre and post-emergence herbicide to control annual grasses and broadleaf weeds in the field and vegetable crops. Sorption of herbicide on soil directly or indirectly controls the fate of herbicide, including movement in soil. Metribuzin adsorption is influenced by various soil physical, chemical and physico-chemical properties. Metribuzin sorption behavior is highly correlated with the organic matter, clay content and the adsorption isotherms are well described by the Freundlich equation. The present investigation reports the influence of physico-chemical parameters sorption and leaching of metribuzin. Leaching potential assessment was done by Groundwater Ubiquity Score (GUS) by using The istribution coefficients Kd, Koc for the soils . According to GUS scores S-3 soil sample resulted as non leachable with 1.8 score, S-1 is transitional with 2.22 , S-3 is leachable with 2.88 score.

Keywords: Metribuzin, Sorption, Groundwater Ubiquity Score (GUS)

Introduction

Metribuzin [4- amino - 6 - tert- butyl- 4,5- dihydro-3- methylthio- 1,2,4- triazinone], is a herbicide extensively used for the control of a large number of grassy and broad leaved weeds in crops like sugarcane, maize, wheat and vegetables like potato, tomato and carrot.

Most of these herbicides applied to the soil where they are subjected to physico-chemical, chemical and microbial processes. Among the physico-chemical processes adsorption, desorption, persistence, movement and leaching have been found to be predominant processes influencing the fate of the soil applied herbicides. A herbicide must remain active in soil till the desired effect is obtained and should degrade to safer levels after the desired level of activities. Movement of herbicides both in the form of vertical and horizontal is an important process that determines the amount of herbicide going into the ground water and it's fate in soil and aquatic environment. The available information on the persistence, movement and leaching of metribuzin in different soils is lacking.

Hence the research work is proposed to study the leaching potential of the metribuzin in different soils of Telangana State.

Material and methods:

Physico-chemical properties of soils

Soil samples varying in their physico-chemical properties were collected from different mandals of tomato growing soils of Ranga Reddy district in Telangana state

Particle size analysis of the soil was carried out by Bouyoucos hydrometer method . pH and electrical nductivity (EC) were measured in 1:2.5 soil water extract. The soil samples collected were analyzed for organic arbon (%), based on rapid titrimetric method. . The details of the soil samples collected and their physico-chemical characteristics are presented in Table 1.

Adsorption

Adsorption studies were carried out in all the 30 soil samples collected from the farmer's fields. Adsorption – Desorption studies were carried out in three selected samples of farmers. Five grams of soil was equilibrated with 20 mL of metribuzin solutions of various concentrations ranging from 0 to 50 µg mL-1for 24 hours with intermittent shaking at constant temperature of 270C. CaCl2 of 0.01M concentration was used to maintain the ionic strength. After 24 hours, the slurry was centrifuged at 4,000 rpm for 15 minutes. Identical soil blanks were maintained (without addition of herbicide). The absorbance for each treatment and corresponding blank values were measured at 455 nm. The difference between the treatment and blank was taken as actual equilibrium absorbance for which the concentration was calculated with reference to the calibration curve. Using the difference between initial and equilibrium concentration the amount of herbicide adsorbed per gram of soil was calculated.

Quantitative treatment of adsorption data
The commonly used mathematical model, Freundlich isotherm equations are used in this study to explain isotherms
Freundlich adsorption equation
The equation may be expressed as
$x/m = K_f . C^{1/n}$
x/m = Amount adsorbed per unit mass of adsorbent
C = Equilibrium concentration
K_f = Freundlich constant related to the strength of binding
n = Constant which is less than 1
The constant K_f is related to strength of binding and depends on temperature.
K_f and n are determined from a logarithmic transformation of the equation, which is linear,

$$\text{Log } x/m = \text{Log } (Kf) + l/n . \log (C)$$

The constant K_f and n were determined from the plot of log x/m vs. log C, the intercept and slope being log K and 1/n, respectively.
Hamaker and Thomson (1972) gave a relationship to describe the distribution of soil adsorbate between two phases, as simple partitioning between soil and water.

$$x/m = K_d . C$$

Where,
x/m is the concentration of the adsorbate in μg g^{-1}
K_d is the soil – water distribution co-efficient.
C is Equilibrium Concentration μg mL^{-1}

The soil-water quotient was calculated as

$$Kd = \frac{\text{Amount adsorbed } (\mu g\ g^{-1})}{\text{Equilibrium Concentration } (\mu g\ mL^{-1})}$$

The soil organic carbon- water quotient was calculated as

$$K_{doc} = \frac{K_d}{\%\text{ Organic carbon}} \times 100$$

Persistence:
A known quantity of 2 mm sieved soil samples were spread on paper and treated with metribuzin. Metribuzin was dissolved in methanol in order to get a concentration of 10 μg L^{-1}. This was sprayed on the soil sample and then methanol was allowed to evaporate. Ten gram portions of herbicide treated soil samples were weighed in to polythene bags and the polythene bags were sealed after adding pre determined quantities of water to bring the moisture levels to field capacity. Duplicate soil blanks without the herbicide were maintained simultaneously.
The samples after moisture treatment were incubated at 27$\pm$ 0.2 °C and the soil samples were analyzed at 0, 1, 3, 5, 7, 10, 15, 30, 45, 60, 75, 90 and 105 days intervals for the amount of herbicide retained in the soil solution. For this soil sample collected at each interval was extracted with methanol to measure the quantity of herbicide extracted. The individual soil samples at each interval was transferred to 60 mL capacity screw capped test tubes and shaken with two 20 mL portions of methanol for 30 minutes on mechanical shaker and filtered through Whatman No 1 filter paper. The standard solutions were transferred quantitatively into reaction flasks, followed by the addition of 10 mL of DMAB (0.04 mol L^{-1}) and 2 mL of NaOH (0.87 mol L^{-1}) solutions. The solutions were heated at 80 °C for 4.0 minutes on a water bath. The solutions were then acidified with 2 mL of 2.8 mol L^{-1} hydrochloric acid solution and continued heating further for 1.0 min more. After cooling, the solutions were diluted to 25 mL with distilled water and allowed to stand for 15.0 min. The absorbance of the colored product was measured at 455 nm for metribuzin. The concentrations of metribuzin was determined with reference to the standard curves after correcting the soil blanks.
Leaching potential assessment:
Herbicides can be ranked by two different indices in relation to their leaching potential. In that Groundwater Ubiquity Score is used for assessing the leaching potential of the herbicide metribuzin.
(GUS) is defined by:

$$GUS = \log t1/2\ (4 - \log Koc)$$

Where,
GUS represents a dimensionless index,
$t1/2$ is the herbicide half-life in soil
$Koc = (Kd/\%OC) * 100)$
Herbicides with GUS < 1.8 are ranked as non-leachers, whereas chemicals with GUS > 2.8 represent leachers. Those with GUS between 1.8 and 2.8 are considered transitional.

Results and discussion:
Adsorption:
The extent of adsorption on the soil samples at initial concentration of 5.0 μg mL^{-1} varied from 0.41 μg g^{-1} to 5.01 μg g^{-1}. In general, the metribuzin adsorption was higher in soils with higher clay content and higher organic matter content. The adsorption was slower at the lower initial concentrations (<15 μg ml^{-1}) and increased rapidly at the intermediate concentrations and tended to slow down at higher concentrations of >40 μg mL^{-1}. These results are in good agreement with the findings of Khoury *et al.* (2003) who found that a clay soil retains more metribuzin than a sandy loam soil. Results of Delle Site (2001) and Singh (2006) also indicated that organic carbon and clay content of the soil positively influence the most metribuzin adsorption.
The distribution coefficients Kd, Koc for the soils are presented in the table 2. K_{oc} values are recorded very high in S-3, medium in S-1, low in S-2. The soil organic carbon-water distribution coefficient was found to be helpful in estimation of the leaching of metribuzin in soil and adsorption properties of the herbicide in soil. The K_{doc} values for metribuzin in soils varied from 33.36 to 140.31. The lowest K_{oc} was noticed in S-2 and highest K_{oc} in S-3. The highest and the lowest K_{doc} values were in close correspondence to the organic carbon content of the soils. These values are in the range of K_{oc} coefficients for metribuzin described by Johnson (2001). The K_{oc} values of metribuzin computed by Bakhsh *et al*. (2004) and Kah and Brown (2007) were 109 and 66 for

different soils. These values were considered to be low, indicating a high risk of mobility of metribuzin. The K_{oc} values reported in the thesis are in agreement with the Koc values between 9 and 120 reported in the literature cited above.

Freundlich equation has been used effectively to determine the adsorption of herbicides on soil, where the fraction of adsorbed herbicide is low (Pandey and Agnihotri, 2000). The co-efficient of determination (R^2 values) for the log x/m and log Ce plots were greater than 0.97, indicating the excellent fit of the adsorption data by Freundlich equation. The values of 1/n suggest the existence of non – linear adsorption. There could be a decrease in available sites as the adsorption increases. This is particularly true in soils with low organic matter and clay content. Another factor that affects the fraction of herbicide adsorbed is the type of adsorption sites. Organic molecules tend to adsorb to high energy sites first followed by the progressively weaker sites (Sonon and Schwab, 1995).

Persistence:

Persistence studied were conducted to study the half life of the herbicide metribuzin. The half life of the metribuzin in S-1 soil is 30 days and S-2, S-3 soil samples are 15 days. The amounts of methanol extractable metribuzin at different time intervals are given in table 3 .

Conn *et al.* (1996) reported that the initial dissipation of metribuzin was rapid in silt loam and sandy loam soils. They found that 35 days after application an average of 24 % initial applied metribuzin remained in the soil. An average of 19% metribuzin remained in the soils even after 105 days after application. Persistence pattern of metribuzin obtained in the study is in close correlation with these findings. Persistence pattern observed in the study is similar to herbicide disappearance behavior observed by Arvind *et al.* (2000); Kewat *et al.* (2001); Brar *et al.*(2005). Rapid dissipation of other groups of herbicides in the initial period has been reported previously by several workers (Savage, 1977; Patel *et al.*, 1996).

Leaching potential

Groundwater Ubiquity Score (GUS) is used to assess the leaching potential of metribuzin in these soils. The distribution coefficients Kd, Koc, Groundwater Ubiquity Score (GUS) for the soils are presented in the table 2.Based on half life and the *K*oc values obtained for the three soils GUS Score was calculated. According to GUS scores S-3 soil sample resulted as non leachable with 1.8 score, S-1 is transitional with 2.22 , S-3 is leachable with 2.88 score.

Conclusion:

The three soil samples collected from different places which are applied with metribuzin were analysed and concluded that there is a variation in the leachin potential in these soils. According to GUS scores these soil samples are classified as S-3 soil sample resulted as non leachable with 1.8 score, S-1 is transitional with 2.22 , S-3 is leachable with 2.88 score.

Table 1: Physico-chemical properties of soils

S No	pH	EC (dS m^{-1})	CEC mol(p+) kg^{-1}	OC (Mg/m^3)	Particle size distribution (%)			Texture
					clay	silt	sand	
S-1	8.84	0.27	31.3	0.94	43.7	30.2	26.1	Clay
S-2	6.52	0.13	13.91	0.32	15.8	13.5	70.7	Sandy loam
S-3	8.17	0.42	24.2	0.47	31.1	34.2	34.7	Clay loam

Table 2: K_d , K_{oc} GUS values of metribuzin adsorption on soil samples

S No	OC (Mg/m^3)	K_d	K_{oc}	GUS
S-1	0.94	0.70	127.1	2.22
S-2	0.32	0.11	35.48	2.88
S-3	0.47	0.60	74.64	1.80

Table 3: Amount of methanol extractable metribuzin at different day intervals, moisture levels (µg /10 g) soil in selected soil sample (S-8)

Days	S-1	S-2	S-3
0	105.12	100.62	95.64
3	82.82	78.85	85.14
5	67.71	66.34	79.36
9	54.63	52.21	66.83
15	42.12	40.26	55.31
30	37.65	36.12	38.48
45	35.21	32.85	36.21
60	32.71	31.24	35.38
90	31.42	27.12	33.90
115	27.35	26.25	32.59
135	31.45	26.41	26.23

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