METRIBUZIN MOBILITY IN SOIL COLUMN AS AFFECTED BY ENVIRONMENTAL AND PHYSICO-CHEMICAL PARAMETERS IN MUMIAS SUGARCANE ZONE, KENYA

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ABSTRACT

The physico-chemical parameters of soil, influences the soil solution characteristics and that may affect the sorption of soil applied herbicides. The present investigation reports the influence of physico-chemical parameters sorption and leaching of metribuzin, a triazine herbicide. The K_f (Freundlich adsorption coefficient) values of metribuzin were 14.9 µg/K which suggests that sorption as a function of herbicide concentrations and (1/n) value of 0.20 µg/L reflecting the degree of sorption of the herbicide. For leaching the amounts of metribuzin leached were 89.83% of applied quantity this is due to effects of various physicochemical factors and climatic conditions in tropical soils. The study concludes that less than 10.17% of applied metribuzin remains in the soil. However from agricultural point of view, the amounts are trivial, but from environmental (including potential ground water contamination) point of view, small residues are important factors to consider.

Keywords: metribuzin, sorption, leaching, tropical soils.

INTRODUCTION

Leaching of soil applied pesticides is considered to be the main source on non-point contamination of ground water. Metribuzin (4-amino-6-tert butyl-3-methylthio-1,2,4-triazin-5-one), a triazine, is used as a selective herbicides for pre and post emergence control of annuals grasses and broadleaf weeds in sugarcane, soybean, wheat etc. triazine herbicides are weakly basic in nature and can be sorjbed to both soil organic carbon and clay minerals. [1-2] with sorption increasing slightly as the soil pH is decreased [3]. The solubility of metribuzin in water is 1.2g/L at 20^0C, its vapour pressure at 20^0C is less than 1.3×10^{-3} pa [4]. The extents to which metribuzin leaches to ground water is inverse function of organic matter content of soil. Its half life in soil ranges between 2.5 and four months [5]. Its half life in pond water is approximately seven days [6]. The extent of herbicide leaching depends on the properties of both soil and herbicide as well as on soil management practices such as application of compost and fertilizers which is an integral part of today's extensive agriculture. Sorption of soil-applied herbicide can be influenced by soil solution characteristics, thus application of fertilizers affect the sorption and mobility of herbicide [5, 7, and 8]. Previous researchers [9-12] have indicated that soil organic carbon content is largest single factor responsible for metribuzin sorption in soils. There have been several reports on metribuzin mobility in soils. Hyzak and Zimdahl [13] reported that most soil-applied metribuzin was found in upper 5cm of the profile even after 24.4 cm of precipitation during a 12 month period. However, contrary findings were reported by others. [9, 14, 16] Kim and Feagley [15] reported that, when soil columns were leached with three pore volumes of water, 88.6% of metribuzin appeared in the leachate. Bedmar *et al*., [16] reported that, after 90cm irrigation, 97.3% of column applied metribuzin was recovered from leachate. There has been no report on the effect of environmental physico-chemical parameters on tropical Mumias sugarcane soils of Kenya. The present highlights the effect of Environmental and Physico-chemical parameters on sorption and leaching of metribuzin in packed columns of Mumias soils.

MATERIALS AND METHODS

Metribuzin (99.8% in purity) was obtained from Kobian Kenya Limited, other reagents used include Dichloromethane, Acetone, Calcium Chloride, Florosil, Sodium Sulphate and acentonitile, all obtained from Kobian Kenyan limited. The instruments used were HPLC machine, Model Shimadzu Comp. CMP - 20AC (120234532), Eyela digital Rotary Evaporator N - 1000, Rotary shaker (SOI UK), and centrifuge universal 16®. The soil samples were obtained from the plough layer 0-20cm of four surfaces field in Mumias Nucleus Zone, Western Kenya (FAO 1977), samples were mixed and dried sieved Through a 2mm mesh. The soil properties were determined (Walker *et al*., 1939), which are summarized in Table-1. The effect of metribuzin concentration in adsorption were monitored as follows: - $0.01CaCl_2$ aqueous solution (25ML) containing standard metribuzin (99.8%) concentrations ranging from 0.1ppm to 5ppm at a desired pH of 5.4. were added to soil samples (5g in triplicates in 50ML pyrex conical flask). The samples were shaken on rotary shaker (Sol UK) at l00rpm at room temperature (28 + or - 2°C) for 2, 4, 6 and 16 hours. After equilibrium, they were centrifuged for 5 min at 300rpm at 27°C using universal 16® centrifuge.

The supernatant were collected in 50ML flask and soil residues were put and preserved in dark polythene bags and covered using aluminum foil. The supernatants were partition in dichloromethane 30ML thrice, collected and evaporated to dryness using Eyela Digital rotary evaporator N-1000, rinsed and made up to 2ML. The 5ML samples were cleaned up with 5g Florosil, 2g of Na_2SO_4, packed in 10cm diameter column using 50ML dichloromethane. The leachate collected and rotary evaporated to 2ml and taken for HPLC analysis.

For leaching experiments were performed using a glass column (45cm diameter, 38cm long), 4g of standard metribuzin was loaded in the column and the column left to leach for 9 hours drained with 1.94 liters of 0.1M $CaCl_2$ at flow rate of 3.6 ML/min. the leachate was measured and partition with 250ML dichloromethane in 2 Liter leachate. The partition sections were subjected to the same experimental procedure as above. The soil sections were carefully removed into divisions of 0-5, 5-10, 10-15, 15-20, 20-25, 25-30 and 30-38cm taken through the same experiment procedures as Adsorption.

All HPLC measurements were made using Shimadzu HPLC machine, the parameters for chromatographic determination of metribuzin were as follows: injection loop volume 10µl Elution condition with 99% acetonitrile at room temperature, flow rate 1.5ML per min and a UV detector at wavelength of 254nm. The identification of metribuzin was done by comparing the retention times of sample extract peaks with the authentic pure standard. Calculations were done by using calibration curve. $Y = 14556X + 7938$ (R^2 0.9)

RESULTS AND DISCUSSIONS

Physicochemical parameters

Table-1 shows the soil characteristics of Mumias soils; Table-2 shows physico-chemical parameters of metribuzin herbicide.

Table-1. Soil properties of Mumias soils.

Soil	% Clay	% Sand	% Silt	pH (H_20)	% Organic carbon	Pb	Cu	% Moisture content
Mumias	9.6	66.4	24.0	5.4	8.2	5.2785	6.289	25.2

Table-2. The selected physico-chemical properties of Herbicide metribuzin.

Herbicide	Formula	Molecules weight	Mp	K_{oc}	Vapour vressure	Solubility in water
Metribuzin	$C_8H_4N_4OS$	214.3	125-126.5	95	1.3×10^3pa	1.2 Kg at 20 °C

As it was expected, the difference in soil characteristics in Mumias soil will have an effect on adsorption and leaching of metribuzin. However it was noted that a marked difference in relationship between adsorption and leaching with organic matter content was observed as earlier been noted by Peter *et al*., [9], Savage [25] and Sharom *et al*., [5] high moisture content of 25.2% favored formation of metabolic deamino-metribuzin (DA), hence less percentage of recovered residues noted in soils. Khoury *et al*., [11]. The high percentage of sand (66.4%) and relative high percentage of clay (9.6%) and silt (24.0%) helps in faster degradation of metribuzin, also noted by Locke *et al*., [29] and Happer [10]. A PH of 5.4 (acidic medium) did favor the recoveries of small quantities of residues as reported by Kearney *et al*., [26].

Environmental factors

The High air and soil temperatures of 28^0C favored the degradation of metribuzin and had demonstrated a linear relationship with degredation as also reported in Hyzack *et al*., [13] Table-3.

Table-3. Comparative weather report during the month of April-June 2006.

Weather element	April - June 2006	Median
Daily maximum air temperature	26-32ºC	28ºC
Daily minimum air temperature	12 - 18ºC	15ºC
Daily wind speed	60 - 120KPH	80KPH
Daily evaporation rate	0 - 15mm	4.5mm
Daily humidity (9.00am)	62 - 90%	80%
Daily relative humidity (5.00p.m)	32 - 85%	55%

The rapid dissipation of metribuzin may also have been influenced by laboratory and field weather conditions and hence be explained by rapid volatilization (note daily evaporation rate of 4.5mm) and biodegradation. Microbial degradation is also the principal route of removal of metribuzin. Pritchard [27] reported that the rapid detoxified by deamination by the soil fungus

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cunninghamella echinuleta, which is highly favored by high temperatures of 28^{0}C noted.

Analysis of variance

The analysis of variance showed there is a difference in 0.1, 1, 2 and 5ppm concentration of adsorbed metribuzin. And that it showed slopes at 95% confidence levels. The Pearson's correlation coefficient of 0.1066774, which is in a good agreement with studies made by Harper [10].

Adsorption

Table-5 shows the actual recovery data for metribuzin through out the study period and Table-6 shows calculated amounts adsorbed.

Table-5. The actual recovery data for Adsorption of metribuzin.

Volume dosed µL	**Amount dosed in 25ML $CaCl_2$**	**Time in hours**	**Amount adsorbed in soil µg/g** (x/m)	**Amount in water** (µg/L) **C**	**Log x/m**	**Log C**	**Amount in mol/Kg**
2.5 µl	0.1873	2	6.68E-03	2.499	-2.1752	0.3977	9.99
2.5 µl	0.287	4	0.02234	2.497	-1.6509	0.3974	9.98
2.5 µl	0.441	6	0.05121	2.448	-1.2906	0.3888	9.91
2.5 µl	0.1097	16	0.06003	2.439	-1.2216	0.3872	9.75
25 µl	0.6039	2	0.04497	24.95	-1.347	1.397	99.8
25 µl	1.08	4	0.04783	24.95	-1.3202	1.397	99.8
25 µl	2.314	6	0.08383	24.91	-1.0766	1.3963	99.6
25 µl	1.966	16	0.04724	24.95	-1.3256	1.397	99.8
50 µl	0.578	2	0.03562	49.96	-1.4483	1.3986	199.8
50 µl	1.2741	4	0.07894	49.92	-1.1027	1.6982	199.6
50 µl	2.065	6	0.09039	49.9	-1.0438	1.6981	199.6
50 µl	1.423	16	0.0502	49.94	-1.2992	1.6984	199.7
125 µl	1.9254	2	0.05046	124.94	-1.297	2.0967	499.7
125 µl	2.0838	4	0.05187	124.94	-1.285	2.0967	499.7
125 µl	2.1816	6	0.05707	124.94	-1.2435	2.0967	499.7
125l µl	1.3764	16	-3.593	125	-0.5554	2.0969	500

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Table-6. The calculated amount of metribuzin adsorbed in mumias soil.

Concentration (PPM)	**Time** (Hours)	**A**	**B**	**C**	**Mean**	**STDEV**
0.1	2	-7.80E-03	0.0109	-7.70E-03	-0.00153	0.010768
0.1	4	0.0229	0.0177	0.01976	0.02012	0.002619
0.1	6	0.0739	0.0742	0.071	0.073033	0.001767
0.1	16	0.1119	0.1122	0.0435	0.0892	0.039578
1	2	0.0614	0.0616	0.0618	0.0616	0.0002
1	4	0.06768	0.0681	0.0647	0.066827	0.001854
1	6	0.0802	0.0835	0.2348	0.132833	0.088321
1	16	0.0708	0.0647	0.0617	0.065733	0.004637
2	2	0.0448	0.0459	0.04274	0.04448	0.001604
2	4	0.0762	0.0679	0.0775	0.073867	0.001604
2	6	0.144	0.1472	0.1435	0.1449	0.002007
2	16	0.0745	0.068	0.071	0.071167	0.003253
5	2	0.072	0.07108	0.072	0.071693	0.000531
5	4	0.075	0.07423	0.07349	0.07424	0.000755
5	6	0.0828	0.0858	0.08274	0.08378	0.00175

For adsorption the K_f values were 14.9 µg/K, which represents the amount of metribuzin adsorbed at 1mg/K. The (1/n) value of 0.20 µg/L, which is near to unity and explains the degree of sorption as a function of herbicide concentrations. (Giles *et al*.,) [28] noted in Table-7 and Figures 1 and 2.

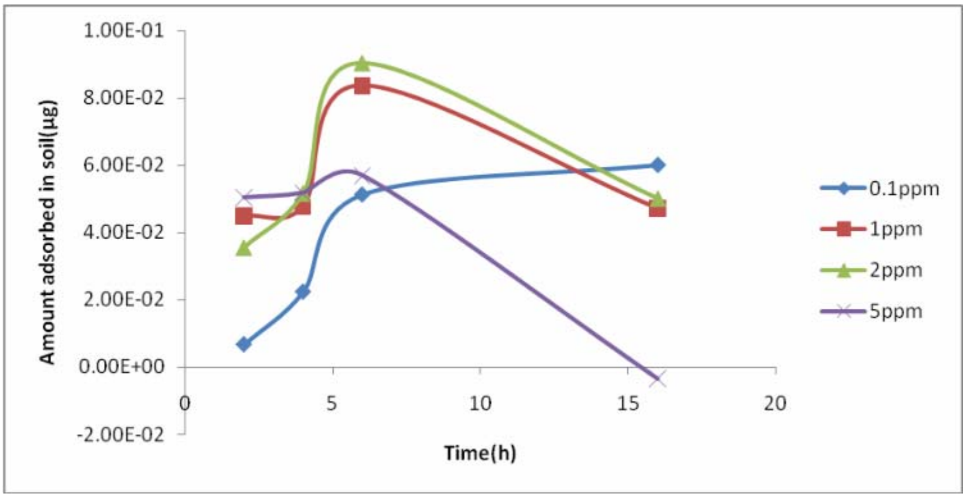

Figure-1. Freundlich adsorption data for mumias soil.

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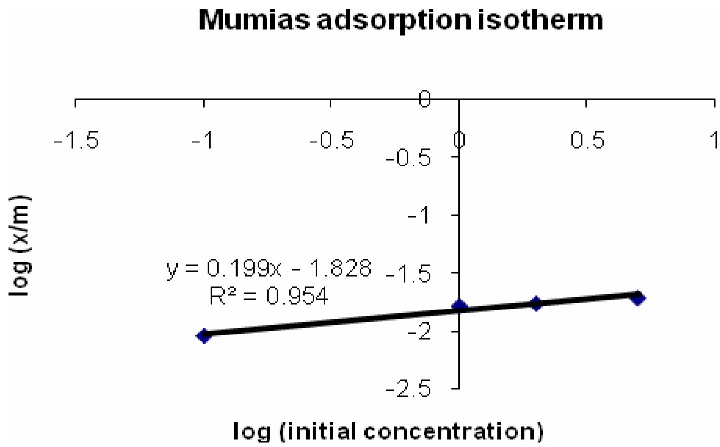


Figure-2. Metribuzin adsorption curve log c versus log x/m at equilibrium concentration.

Table-7. Adsorption parameter formumias soils.

1/n(µg/L)	R^2	K_f(µg/kg)	K_{oc}(µg/kg)
1.096	0.924	0.112	0.292

The measurement of metribuzin were fitted to Freundlich adsorption equation;

Log (x/m) = log K_f + (1/n) logC

Where x/m is the concentration of herbicide sorbed on soil (µg/g), C is the solution concentration of herbicide (µg/L) and K_f and 1/n are Freundlich constants (Figure-1). It was noted that S type of isotherms fitted well to all the four concentrations Giles *et al*., [28].

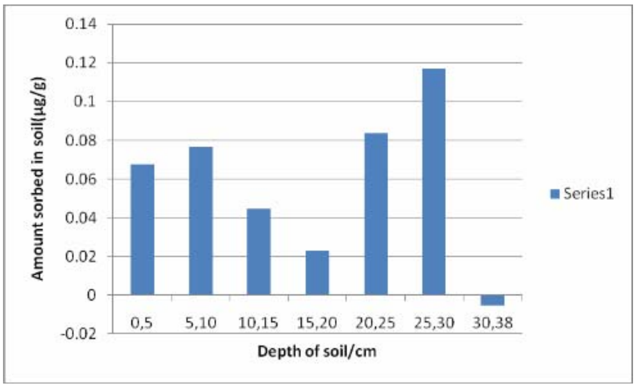
The Freundlich adsorption coefficient (K_f) represents the sorption of Metribuzin at an equilibrium concentrations of 1µg mL^{-1} while (1/n) (slope) reflects the degree to which sorption is a function of herbicide concentration. The adsorption data were fitted to the Freundlich equation, with correlation coefficient (r^2) values of 0.954 which further confirms the S type model of isotherm proposed earlier. Table-7 confirms that metribuzin was weekly sorbed. The reported K_f values in this study are in agreement with earlier reports [20, 21], which show poor retention of metribuzin in sandy warm soils of mumias. The K_{oc} values were 182 (µg/kg) which is a universal parameter for describing adsorption.

Leaching studies

Table-8. Data for leaching studies of metribuzin.

S. No.	**Column** (cm)	A	B	C	Mean	STDEV
1	0,5	0.06905	0.06589	0.06819	0.06771	0.00163377
2	5,10	0.0777	0.07515	0.0778	0.076883	0.00150194
3	10,15	0.04335	0.04362	0.04677	0.04458	0.00190139
4	15,20	0.026	0.01842	0.0248	0.023073	0.00407433
5	20,25	0.08586	0.08145	0.08402	0.083777	0.00221505
6	25,30	0.11252	0.116	0.12216	0.116893	0.00488169
7	30,38	ND	ND	ND	ND	ND

The distribution of metribuzin in sections of the soil columns is shown as total amount adsorbed in µg/g which are expressed into percentage against amount applied. The recovery in soil was 10.17%; however these percentages are expressed in equivalent µg/L of Metribuzin. The experiment lasted for 9 hours. Figure-3 shows a correlation of the soil depth in centimeters and the amount adsorbed in soil (µg/L) hence, 0-5cm had (0.06771); 5-10cm (0.07688), 10-15cm (0.04458), 15-20cm (0.02307), 20-25cm (0.68377), 25-30cm (0.1168) and 30-38cm were not detected and had percentage range being from 0.128% to 2.09% distributed in the columns.



Fiqure-3. Distribution of metribuzin with soil depth.

This again suggests that the amounts in soils are trivial and that dissipation of Metribuzin is affected by Environmental as well as physico-chemical parameters.

CONCLUSIONS

The study concludes that Metribuzin is weakly adsorbed in soil K_f 14.9 µg/K and (1/n) 0.20 µg/L reflecting a degree of sorption. The amount leached is more than 90% and the remaining residues are less than 10%. Many authors have noted the same. Although metribuzin is a potential environmental factor, and causes deleterious effect to Biota in large quantities. It is concluded however, that the small quantities left in the Mumias soil due to effect of tropical environments and physico - chemical factors might not cause detrimental changes in the surrounding environment but may cause pollution of water aquifers.

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