Adsorption of Atrazine and Terbacil by Soils

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INTRODUCTION

The adsorption of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (Atrazine) and 3-tert.-butyl-5-chloro-6-methyl uracil (Terbacil), by soils has been studied by a number of research workers (*1,2,3,4,5,8,9,10*).[2] Information concerning such adsorption under tropical conditions is wanting. Such information is essential for understanding the behavior of such compounds in the soil. Data was presented in a previous publication (*7*) concerning the adsorptive capacity of 34 native soils of two of our most currently used herbicides, 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine (Ametryne) and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron). Data also was presented concerning the effects of various environmental factors upon the adsorption characteristics of these two herbicides. In the present study, Ametryne and Diuron were substituted by Atrazine and Terbacil. Atrazine is used extensively to control noxious weeds in various crops of economic importance of Puerto Rico including sugarcane (*Saccharum officinarum*). Terbacil shows promise for control of weeds in sugarcane.

MATERIALS AND METHODS

Samples from the upper layer (15 cm.) of 34 soil types were collected from various regions of Puerto Rico representing a wide variety of climatic and edaphic conditions. The samples were air-dried, ground and passed through a 0.25-mm. screen. The physical and chemical properties of these soils were determined by methods similar to those employed previously (*6*).

To determine the extent to which Atrazine and Terbacil were adsorbed by each soil, the radioassay procedure outlined by Talbert and Fletchall (*10*) was followed. Stock solutions (concn. 1 p.p.m.) containing either ring-labeled C^{14}-Atrazine (specific activity 10.1 μc./mg.) or 2-C^{14}-Terbacil (specific activity 4.13 μc./mg.) were prepared with 0.01 *M* $CaCl_2$ in 1,000-ml.

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[2] Italic numbers in parentheses refer to Literature Cited, p. 460.

volumetric flask. Five ml. of each herbicide were added from stock solutions to Erlenmeyer flasks containing soil samples. The flasks were stoppered and agitated in a reciprocal shaker at room temperature for 24 hours. Individual samples then were transferred to 15-ml.-capacity glass tubes and centrifuged for 20 minutes at 5,000 r.p.m. Subsequently, 0.5 ml. of the supernatant was removed and placed in a glass-counting vial. Ten ml. of liquid scintillator (0.4 percent 2,5-diphenyloxazole and 0.01 percent 1,4 bis-2-(5-phenyloxazole)-benzene in 1,000 ml. of toluene) were added to each vial. Each vial then was placed in a Beckman model automatic liquid scintillation spectrometer for a 5-minute count. Five ml. of blank standards with a series of known concentrations (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 p.p.m.) were included in the study and used for plotting the standard curve for each herbicide. The concentration of herbicide remaining in solution for the various soil samples was estimated by fitting the radioactivity measured in the aqueous solution of these samples to that of the standard curve. The difference between the original concentration and residual concentration represents the amount of herbicide adsorbed by the soil. All determinations were made in triplicate.

For making the adsorption isotherms studies, one g. of air-dried soil was placed in an Erlenmeyer flask with 5 ml. of stock solution of different initial herbicide concentrations (0.625, 1.25, 2.5, 5.0 and 10.0 p.p.m. for Atrazine; 0.3125, 0.625, 1.25, 2.5 and 5.0 p.p.m. for Terbacil). The same methodology employed in the first phase of the adsorption study was used again. Adsorption isotherms were prepared by plotting the amount of herbicide adsorbed against the herbicide concentration in the equilibrated solution. Each point on the adsorption isotherms represented the average of three determinations except that only duplicate determinations were made with the highest concentration of Atrazine (10 p.p.m.).

RESULTS

The physical and chemical properties of the 34 soils used in the study are presented in table 1. The observed and estimated adsorption percentage for Atrazine and Terbacil in 34 soils are presented in table 2. Caño Tiburones soil manifested considerably higher capacity for adsorption of Atrazine and Terbacil than all other soils, whereas, Toa sandy loam showed the lowest adsorptive capacity for Atrazine and Talante sandy loam for Terbacil. Adsorption of Atrazine and Terbacil by other types was between these two extremes. It is significant to note that the adsorption of Atrazine and Terbacil appeared to be relatively low when compared to that of Ametryne and Diuron (table 3). Thus, the relative adsorptivity of these soils for the herbicides is the following: Diuron > Ametryne > Atrazine > Terbacil. Harris (*2*) and Talbert (*10*) also reported the low adsorption

TABLE 1.—*The chemical and physical properties of 34 Puerto Rican soils*

Soil name	P p.p.m.	pH	Meq. per 100 g.				Percent			
			CEC	Ca	Mg	K	OM	Sand	Silt	Clay
Aguadilla loamy sand	17	7.4	10.0	17.1	3.3	0.20	2.5	74.4	19.5	6.1
Aguirre clay loam	22	9.0	14.3	18.3	28.8	1.44	1.3	27.6	35.6	36.8
Alonso clay	4	5.1	13.8	5.4	2.0	0.91	3.2	14.9	39.3	45.8
Altura loam	33	8.0	27.6	32.2	7.8	1.94	3.7	49.2	28.8	22.0
Bayamón sandy clay loam	6	4.7	5.0	2.7	1.5	0.19	1.7	68.1	4.4	27.5
Caño Tiburones muck	6	5.5	86.0	61.9	14.0	0.80	36.0	36.0	36.0	28.0
Catalina clay	1	4.7	11.8	0.7	0.6	0.08	1.9	6.6	28.9	64.5
Cataño sand	14	7.9	6.9	—	0.2	0.15	2.1	89.0	7.3	3.7
Cayaguá sandy loam	4	5.2	7.3	32.2	7.8	1.94	2.0	58.8	23.4	17.8
Cialitos clay	5	5.4	18.6	6.9	7.0	0.54	4.9	13.3	34.8	51.9
Coloso clay loam	8	5.7	23.0	14.9	5.8	0.15	3.7	22.7	37.4	39.9
Coto clay	13	7.7	14.0	16.6	0.7	0.35	3.2	23.4	24.8	51.8
Fe clay loam	13	7.5	27.6	8.7	20.8	0.81	3.4	39.1	29.7	32.2
Fortuna silty clay loam	5	5.4	23.3	9.2	10.1	0.15	3.3	15.0	50.7	34.3
Fraternidad clay	15	6.3	36.0	24.0	10.4	0.46	2.1	15.5	32.5	52.0
Fraternidad clay (Lajas Substation)	33	5.9	58.0	27.6	19.0	0.65	4.2	11.1	23.8	65.1
Guánica clay	36	8.1	52.1	41.5	37.7	2.58	4.8	6.4	19.6	74.0
Humata silty clay loam	4	4.5	10.1	2.2	0.9	0.27	1.7	10.1	50.9	39.0
Josefa silty loam	5	6.0	16.8	7.4	9.5	0.22	3.3	26.6	53.5	20.9
Juncos silty clay	9	6.2	13.4	16.6	28.8	0.17	2.7	15.2	41.6	43.2
Mabí clay	16	7.0	55.2	19.1	43.7	0.50	3.9	19.9	33.4	46.7
Mabí clay loam	3	5.7	31.0	11.5	14.2	0.56	4.9	22.7	40.7	36.6
Mercedita silty clay	25	8.1	19.9	49.9	9.9	1.02	2.4	14.9	42.8	42.3
Moca clay	6	5.8	31.0	23.4	4.7	0.22	3.8	26.3	27.7	46.0
Múcara loam	6	5.8	19.6	13.6	7.8	0.14	3.3	28.0	47.0	25.0
Nipe clay loam	2	5.7	11.9	4.4	2.5	0.05	5.3	22.0	49.2	28.0
Pandura sandy loam	5	5.7	7.7	5.5	2.4	0.13	2.0	59.4	28.2	12.4
Río Piedras silty clay	4	4.9	11.5	3.9	2.0	0.08	3.5	13.4	43.6	43.0
San Antón loam	16	6.7	26.1	23.8	5.9	0.58	2.7	24.3	49.7	26.0
Talante sandy loam	7	5.1	4.0	0.9	0.2	0.17	1.4	73.4	19.4	7.2
Toa loam	2	5.3	13.0	6.9	1.5	0.23	2.0	41.5	38.3	20.2
Toa sandy loam	8	6.0	8.0	6.2	1.4	0.17	0.6	60.9	25.1	14.0
Vega Alta sandy loam	2	5.0	5.6	1.1	1.3	0.02	3.5	73.7	12.6	13.7
Via loam	3	5.1	39.9	3.9	3.5	0.10	2.3	45.2	36.8	18.0

of Atrazine as contrasted with other herbicides of the s-triazine family. As to Terbacil, Rhode *et al.* (*9*) found the adsorption of this herbicide to be only slightly greater than that of 5-bromo-3-sec-butyl-6-methyluracil (Bromacil) but appreciably less than that of other triazine and urea herbicides he investigated. The low adsorptive capacity of soils for Terbacil,

TABLE 2.—*Observed and estimated adsorption percentage for Atrazine and Terbacil in 34 Puerto Rican soils*

Soil name	Adsorption percentage					
	Atrazine			Terbacil		
	Observed	Estimated	Difference	Observed	Estimated	Difference
Aguadilla loamy sand	10	10	0	5	7	−2
Aguirre clay loam	8	10	−2	8	9	−1
Alonso clay	12	14	−2	5	6	−1
Altura loam	11	15	−4	8	10	−2
Bayamón sandy clay loam	7	5	+2	3	3	0
Caño Tiburones muck	80	—[1]	—	54	—[1]	—
Catalina clay	7	9	−2	4	4	0
Cataño sand	10	7	+3	4	6	−2
Cayaguá sandy loam	7	9	−2	3	5	−2
Cialitos clay	21	20	−1	9	10	−1
Coloso clay loam	19	16	+3	10	8	+2
Coto clay	14	13	+1	8	8	0
Fe clay loam	13	16	−3	11	11	0
Fortuna silty clay loam	20	16	+4	10	8	+2
Fraternidad clay	12	11	+1	8	6	+2
Fraternidad clay (Lajas Substation)	21	18	+3	14	11	+3
Guánica clay	18	21	−3	13	16	−3
Humata silty clay loam	10	10	0	3	3	0
Josefa silty loam	17	16	+1	9	8	+1
Juncos silty clay	18	15	+3	10	9	+1
Mabí clay	22	20	+2	14	14	0
Mabí clay loam	17	21	−4	10	11	−1
Mercedita silty clay	12	13	−1	11	8	+3
Moca clay	19	15	+4	10	8	+2
Múcara loam	14	16	−2	8	8	0
Nipe clay loam	24	22	+2	13	11	+2
Pandura sandy loam	9	9	0	4	5	−1
Río Piedras silty clay	8	15	−7	3	7	−4
San Antón loam	18	14	+4	10	7	+3
Talante sandy loam	6	6	0	2	3	−1
Toa loam	9	10	−1	4	4	0
Toa sandy loam	5	4	+1	3	2	1
Vega Alta sandy loam	14	12	+2	5	7	−2
Via loam	10	11	−1	4	5	−1

[1] Data on Caño Tiburones soil not included in multiple regression analyses.

as noted in this study, is in keeping with the results of Mee (*5*) who observed the same phenomenon in Hawaiian soils.

Adsorption of Atrazine was correlated positively with organic matter content, cation exchange capacity, (CEC) magnesium content, and percent of silt and clay, but negatively with percent of sand (table 4). In a series of multiple regression analyses involving the adsorption percentage and various soil properties, it was found that a combination of organic matter, magnesium and silt offered a basis for the best prediction for adsorption of Atrazine. Consequently, the multiple regression equation $y = -0.031 + 0.107\ (\text{Mg}) + 3.216\ (\text{organic matter}) + 0.088\ (\text{silt})$ was used to calculate the estimated adsorption percentage for Atrazine (table 2).

TABLE 3.—*Observed adsorption percentage for Ametryne and Diuron in 34 Puerto Rican soils*

Soil type	Adsorption Percentage[1]	
	Ametryne	Diuron
Aguadilla loamy sand	22	36
Aguirre clay loam	20	29
Alonso clay	40	35
Altura loam	18	38
Bayamón sandy clay loam	22	22
Caño Tiburones muck	94	98
Catalina clay	20	19
Cataño sand	15	32
Cayaguá sandy loam	27	26
Cialitos clay	56	58
Coloso clay	47	57
Coto clay	18	51
Fe clay loam	25	40
Fortuna silty clay loam	64	59
Fraternidad clay	23	44
Fraternidad clay (Lajas Substation)	44	63
Guánica clay	27	51
Humata silty clay loam	30	21
Josefa silty loam	39	57
Juncos silty clay	51	52
Mabí clay	38	61
Mabí clay loam	34	53
Mercedita silty clay	17	39
Moca clay	57	57
Múcara loam	50	42
Nipe clay loam	48	62
Pandura sandy loam	25	36
Río Piedras silty clay	23	30
San Antón loam	29	63
Talante sandy loam	37	22
Toa loam	48	30
Toa sandy loam	15	15
Vega Alta sandy loam	32	42
Via loam	45	37

[1] The same methodology used for determining the adsorption of Atrazine and Terbacil by the soil was used here.

TABLE 4.—*Simple correlation of soil properties among themselves and with adsorption percentage for Atrazine and Terbacil herbicides using the experimental data from 33 soil types, excluding Caño Tiburones soil*[1]

Factors correlated	P	pH	CEC	Ca	Mg	K	Organic matter	Sand	Silt	Clay
	p.p.m.		*Meq./100 g.*	*Meq./100 g.*	*Meq./100 g.*	*Meq./100 g*	*Percent*	*Percent*	*Percent*	*Percent*
Adsorption percentage for Atrazine	0.167	0.110	0.568**	0.239	0.446*	−0.020	0.810**	−0.528**	0.379*	0.427*
Adsorption percentage for Terbacil	.495**	.446*	.706**	.530**	.666**	.262	.720**	−.558**	.315	.513**
P_2O_5 p.p.m.		.762**	.560**	.777**	.536**	.663**	.154	−.127	−0.223	.324
pH			.269	.667**	.492**	.519**	.057	.025	−0.141	.068
CEC				.489**	.654**	.342	.501**	−.483**	.102	.564**
Ca					.458**	.708**	.177	−.243	−.052	.338
Mg						.490**	.301	−.379*	.064	.455**
K							.163	−.151	−.132	.292
Organic matter (percent)								−.444*	.222	.428*
Sand									.661**	−0.849**
Silt										.164

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[1] * Significant at the 5 percent level
** Significant at the 1 percent level

Adsorption of Terbacil was correlated positively with organic matter, cation exchange capacity, magnesium and calcium content, soil pH, phosphorus content and percent of clay, and again negatively correlated with percent of sand. Similarly, the multiple regression equation $y = -3.20 + 0.675$ (soil pH) $+ 0.121$ (Mg) $+ 1.844$ (organic matter) was derived and used to calculate the estimated adsorption percentage for Terbacil.

To better characterize the adsorption behavior of Atrazine and Terbacil on 12 major sugarcane soils, the empirical constants (K) and lines slopes ($1/n$) of the Freundlich expression

$$\log x/m = \log K + 1/n \log C$$

TABLE 5.—*Freundlich isothermal constants at 1.0 p.p.m. soil solution concentration for 12 Puerto Rican soils*[1]

Soil Name	Atrazine		Terbacil	
	K	1/n	K	1/n
Aguirre clay loam	0.90	0.90	0.72	0.73
Coloso clay loam	2.03	0.93	0.93	0.93
Coto clay	1.20	1.00	0.74	0.90
Fortuna silty clay loam	2.47	0.87	0.97	0.97
Fraternidad clay	1.10	0.93	0.77	1.00
Guánica clay	1.85	0.97	1.50	1.00
Juncos silty clay	2.00	0.87	1.12	0.97
Mabí clay	2.80	0.93	1.65	0.97
Mercedita silty clay	1.20	0.97	1.13	1.00
Moca clay	2.10	0.87	1.32	1.11
Nipe clay loam	2.70	0.93	1.40	0.90
San Antón loam	2.05	0.93	1.18	0.93

[1] Values of K in the table are the values of X/m in μg/g at an arbitrary solution concentration of 1 p.p.m.

Values of $1/n$ are the values of the slopes of the plots of log X/m against log C.

are extrapolated graphically from the adsorption isotherms and given in table 5. Our experimental data generally was found to fit the linearity relationship as shown by the representative adsorption isotherms (figs. 1 and 2). Deviations from linearity were noted with some soils at the lowest concentration for both Atrazine and Terbacil. Hilton and Yuen (*4*) also found a similar type of deviation, especially at the lower Atrazine concentration ranges. As can be seen in table 5, Mabí clay was found to have the highest K values for Atrazine and Terbacil. On the other hand, Aguirre clay has the lowest K values for both herbicides. These various K values, together with their corresponding line slopes, are generally sufficient to characterize the adsorption relationship of Atrazine and Terbacil on a number of our soils. The advantage of using the isothermal adsorption method is that the results obtained are not influenced by soil-herbicide-solution ratios.

SUMMARY

The differential in the adsorption capacity of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (Atrazine) and 3-tert.-butyl-5-chloro-6-methyluracil (Terbacil) by 34 Puerto Rican soils was studied in the laboratory using C^{14}-labeled herbicides. The various soils differed greatly in their capacity to adsorb Atrazine and Terbacil. The Caño Tiburones soil was found to be the most adsorptive for both herbicides; the Toa sandy loam

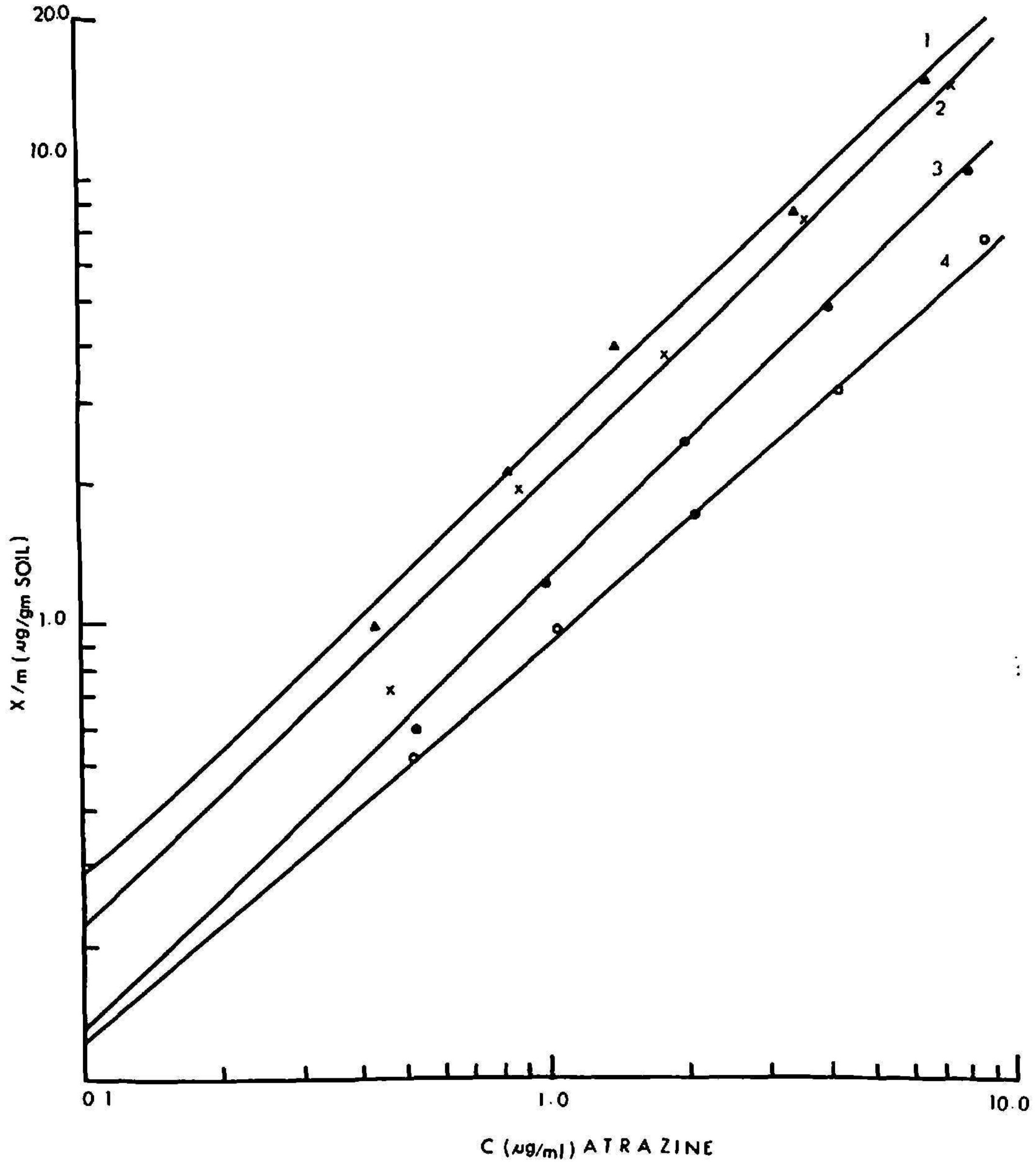

FIG. 1.—Freundlich adsorption isotherm for Atrazine and four soils. From top to bottom: A, Fortuna silty clay loam; 2, Coloso clay loam; 3, Coto clay; and 4, Aguirre clay loam.

and Talante sandy loam the least for Atrazine and Terbacil, respectively. Atrazine was consistently adsorbed to a greater degree than Terbacil. Adsorption of Atrazine was correlated positively with organic matter content, cation exchange capacity and magnesium and silt content but negatively with sand content. Adsorption of Terbacil was positively correlated with organic matter, cation exchange capacity, soil pH, content of phosphorus, calcium, magnesium and clay but negatively with sand content of the soil.

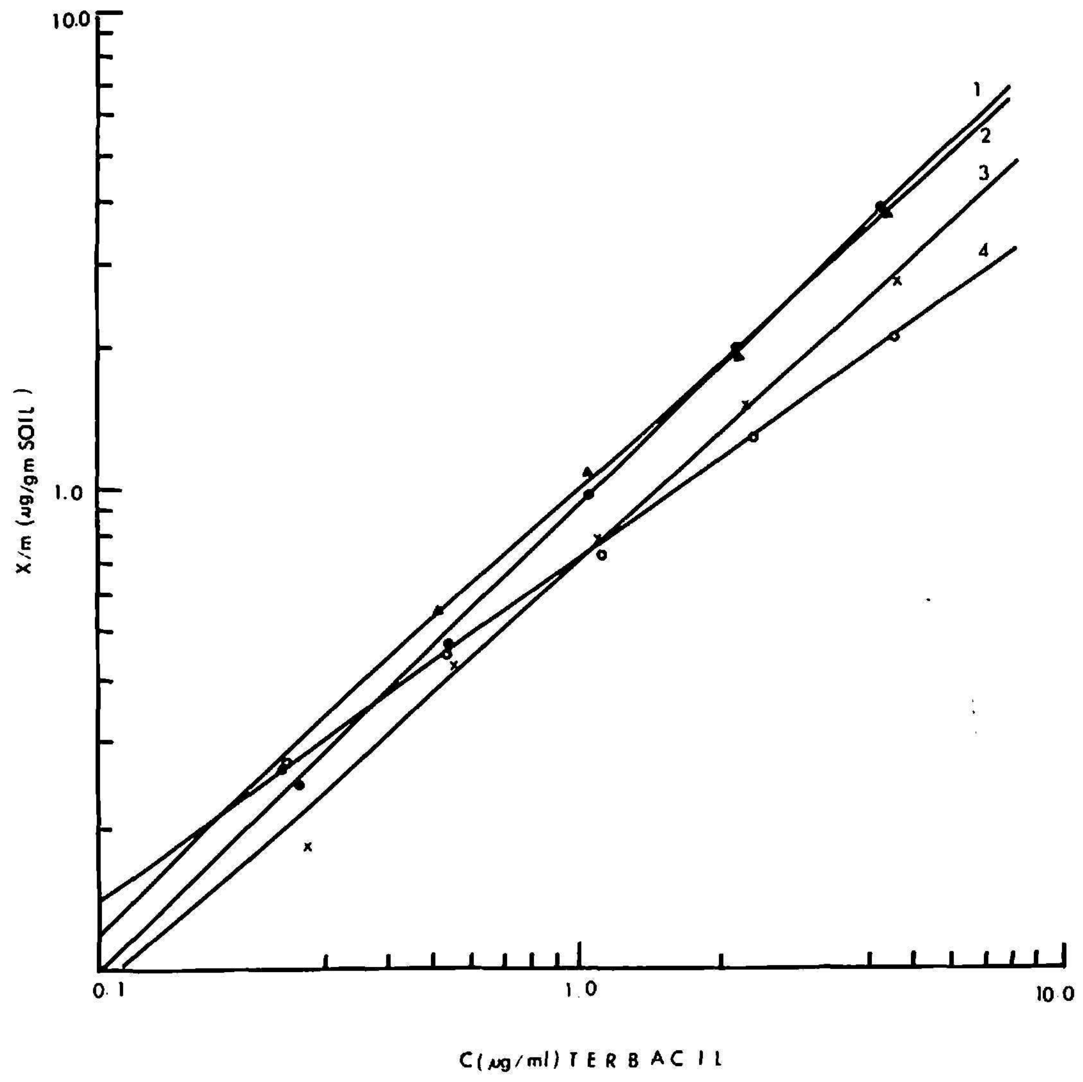

FIG. 2.—Freundlich adsorption isotherm for Terbacil and four soils. From top to bottom: 1, Coloso clay loam; 2, Fortuna silty clay loam; 3, Coto clay; and 4, Aguirre clay loam.

Representative adsorption isotherms of Atrazine and Terbacil on several important island soils devoted to sugarcane cultivation are also presented in this report.

RESUMEN

Se estudió en el laboratorio, mediante el método del carbono (C^{14}), la diferencia en la capacidad adsortiva de 34 tipos de suelos de Puerto Rico respecto a los compuestos 2-cloro-4-(etilamino)-6-(isopropilamino)-s-triacin (Atrazine) y 3-butil-terciario-5-cloro-6-metiluracil (Terbacil). La diferencia en cuanto a dicha capacidad adsortiva fue grande entre varios de los suelos. El suelo Caño Tiburones demostró poseer la mayor capacidad para adsorber ambos yerbicidas, mientras que el Toa y el Talante, ambos margoarenosos, demostraron la menor capacidad para adsorber el Atrazine y el Terbacil, respectivamente. El Atrazine se adsorbió consistentemente en mayor grado que el Terbacil. Se demostró que existía una correlación positiva entre la adsorción del Atrazine y el contenido de materia orgánica, la capacidad para el intercambio de cationes y el contenido de magnesio y limo de los distintos suelos. Sin embargo, dicha correlatión fue negativa respecto al contenido de arena. En cuanto al Terbacil, también se encontró que existía una correlación positiva entre su adsorción y el contenido de materia orgánica, el intercambio de cationes, el pH y el contenido del fósforo, calcio, magnesio y arcilla de los suelos. Como en el caso del Atrazine, la correlación fue igualmente negativa respecto al contenido de arena.

En el estudio también se incluyen isotermos representativos de la adsorción del Atrazine y el Terbacil por varios de los mejores suelos que se dedican al cultivo de la caña de azúcar en Puerto Rico.

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