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AN APPROACH TO THE ADSORPTION OF CHLORPYRIFOS AND DIAZINON IN ANDIC SOILS

Una aproximación a la adsorción de clorpirifos y diazinón en suelos andicos

Edier Humberto Pérez[1], Camilo Andrés Arboleda[2]

ABSTRACT

Not all soils behave equal forehead to the process of adsorption of a pesticide, the soil may minimize or enhance vertical and surface motion thereof, reducing or increasing the possibilities of contamination of groundwater or surface water. The time it takes for pesticides to reach equilibrium with the different phases of the soil is crucial in areas with high intensity and frequency of rainfall. In this case andic soils in areas with these features worked finding that pesticides chlorpyrifos and diazinon reach equilibrium in 12 hours, the adsorption constant (Kf) was calculated using the Freundlich equation and Koc according to the content of organic matter in the soil. In general the adsorption isotherms exhibit good linearity and Koc calculated between 8444-9943 and 5800-6300 for chlorpyrifos and diazinon respectively, these values suggest that both pesticides exhibit strong intensity adsorption on andic soils, this limits leaching processes in soil profile protecting groundwater, but facilitates the processes of surface runoff in dissipation and final fate of these pesticides.

RESUMEN

No todos los suelos se comportan igual frente al proceso de adsorción de un pesticida, el suelo puede minimizar o mejorar el movimiento vertical y de superficie del mismo, reduciendo o aumentando las posibilidades de contaminación del agua subterránea o superficial. El tiempo que tardan los pesticidas en alcanzar el equilibrio con las diferentes fases del suelo es crucial en áreas con alta intensidad y frecuencia de lluvia. En este caso, suelos andicos en áreas con estas características trabajadas encontrando que los pesticidas clorpirifos y diazinon alcanzan el equilibrio en 12 horas, la constante de adsorción (Kf) se calculó usando la ecuación de Freundlich y Koc según el contenido de materia orgánica en el suelo. En general, las isotermas de adsorción exhiben una buena linealidad y Koc calculado entre 8444-9943 y 5800-6300 para clorpirifos y diazinón respectivamente, estos valores sugieren que ambos pesticidas exhiben una fuerte intensidad de adsorción en suelos andinos, esto limita los procesos de lixiviación en el perfil del suelo que protege las aguas subterráneas, pero facilita los procesos de escorrentía superficial en la disipación y el destino final de estos pesticidas.

[1] Doctor en Química, Universidad del Cauca, Grupo de investigación en AgroQuímica. ehperez@unicauca.edu.co

[2] Magister en Ciencias Químicas, Universidad del Cauca, Grupo de investigación en AgroQuímica.

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INTRODUCTION

The use of pesticides and other chemicals for agricultural use appropriately and in the amount indicated is necessary to maintain high agricultural production that is required for the survival of populations. Some authors found that mishandling of pesticides affects ecosystems and human populations that inhabit them, as their organisms are directly or indirectly exposed through the food chain and biogeochemical cycles, thereby pesticide concentrations tend to be higher in places intervened by man with intensive crop and continued spraying[1,2]. Calvet[3], evaluated the adsorption process that occurs between these compounds and soil minimize the vertical and surface movement reducing the chances of contamination of surface or groundwater, this process is defined as the passing of a solute in a liquid or gaseous form to the surface of solid phase without causing changes in the composition of this latter, and is due to the attraction or repulsion between the adsorbent surface (macropores and micropores of soil) molecules or ions of the adsorbate (pesticide). Aguer *et al.*[4] abridge what Adsorption also catalyzes the chemical degradation processes and photolysis, but also protects the adsorbed pesticides of the abiotic and photochemical degradation. Adsorption is affected by several factors, of which the most important are the properties of the contaminant compound (for example, molecular structure, charge, polarity and solubility in water) and soil properties (for example, clay content and organic compounds, pH, moisture and temperature). Generally, an increase in temperature or humidity resulting in a lower adsorption of the contaminant by the soil and a greater contact surface of the solid (fine fractions or colloidal fraction, both organic and inorganic) facilitates greater adsorption capacity. Sukul and Spiteller[5], showed that Furthermore desorption increases the volatilization, bioavailability and transport of pesticides that determine the amount present in the soil solution and therefore control the dynamic of pesticide.

According Gevao *et al.*[6], know the different interactions responsible for adsorption, allows more and better understanding of the process. The physical and chemical forces (protonation, electrostatic bonds, coordination reactions, hydrogen bonding, hydrophobic interactions and ligand exchange) are responsible for the process and its intensity is presented depending on the nature of the functional group and the acidity of the system in which two or more interactions may occur simultaneously. Wauchope *et al.*[7] revises and condenses theory, measurement, uses and limitations of the parameters of adsorption of pesticides in soil is regulator parameter of environmental control agencies to predict the fate and behavior of these compounds in the environment.

Liang *et al.*[8] reported the empirical Freundlich adsorption equation is used to describe the adsorption of organophosphorus pesticides in soil that responds to many experimental results, with no limit on the adsorption. The equation relating the amount of pesticide adsorbed and the amount of pesticide in solution is $\mathbf{C_s = K_f * C_e^{nf}}$ where, Cs: quantity of adsorbed pesticide $\mathbf{C_e}$**:** concentration of the pesticide at equilibrium $\mathbf{K_f}$ and ***nf*****:** constant. The value $\mathbf{K_f}$ comprises the amount of adsorbed pesticide when the equilibrium concentration is half and is considered as the measure of the adsorption capacity of the soil to the particular pesticide and allows comparing the adsorption capacity of different pesticides in different soils. ***nf*** is the slope of the straight and is considered a measure of the intensity of the adsorption, if ***nf*** = 1 Freundlich equation is expressed $\mathbf{C_s = K_f . C_e}$; in this case $\mathbf{K_f}$ coincides with the definition of a distribution coefficient K_d, which is independent of concentration.

Green y Karichoff [9], experienced that for $\mathbf{C_e}$ values different ? to unity, ***nf*** away from the unit and the difference between $\mathbf{K_f}$ and $\mathbf{K_d}$ becomes greater. Lambert[10], studying the importance of organic matter in the adsorption of pesticides poorly soluble in water, used the expression distribution coefficient $\mathbf{K_d}$ in function of organic carbon content of soil by using the equation **Kco = Kd/%CO** with good results. Kodesova *et al.*[11] focused their study on the evaluation of pesticide adsorption process in soils by applying the Freundlich equation, proposing a multiple linear regression to define the prediction coefficient $\mathbf{K_f}$ with organic matter content, pH, CEC and % clay.

Calvet[3], and Dubus *et al.*[11], concluded that the adsorption of pesticides to clay minerals can occur

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mainly in the cation exchange directly or through water molecules coordinated to the cation exchange or by interaction of the basal OH groups of kaolinite and edge of layered silicates.

Chlorpyrifos and Diazinon pesticides, hydrophobic compounds when applied to soils with a content of organic matter greater than 2%, adsorption occurs mainly due to organic matter acts as a means partition; authors as Ahmad *et al.*[12], Nemeth Kunda *et al.*[13], Wauchope *et al.*[7], and Fernández *et al.*[14], consider that there are limitations to attribute to organic matter as the only responsible for the adsorption of polar compounds. Aguer *et al.*[4], working adsorption of organic compounds with polar, ionic or ionizable features, found a higher correlation between adsorption and clay content of soils than with organic matter content. Oliver *et al.*[15], shows how soil use affects the adsorption of pesticides and their metabolites associated with organic matter.

Chlorpyrifos and Diazinon are strongly adsorbed to soil particles and moderately persistent depending on soil type and environmental conditions of the area of application. In EXTOXNET[16] is reported $\mathbf{K}_d$:4.6990, $\mathbf{K}_{co}$: 6070 and a range of half-life ($t_{1/2}$) between 11 and 141 days for chlorpyrifos and for Diazinon $\mathbf{K}_d$: 1000 with ($t_{1/2}$) between 15 and 30 days depending on soil acidity. Spark[17] and Racke[18], Studying the effect of soil composition and dissolved organic matter on the adsorption of pesticides concludes that the factor governing the adsorption is the not dissolved organic matter and clay minerals.

MATERIALS AND METHODS

Location and characteristics of the study area and soil

The area where the soil sampling was conducted is located in the department of Cauca, municipality of Totoro and belongs to the district of Gabriel Lopez. It is located on the central mountain range that corresponds to the Andean region, Calvache wetland, including the geographic coordinates 76.17”51 W, 2.3”34 N. The very cold weather (moor) covering the living area of montane wet forest (bmh-M), affected by frequent frosts and strong winds. Temperatures range from 0-20° C and precipitation ranges between 1200 and 1800 mm per year. The parent material is volcanic ash that covers various geological materials, mainly sand and volcanic tuff.

Soil samples after air dried were sieved to 2 mm and stored at ambient temperature, sealed and labeled. The physical and chemical properties and classification according to Soil Taxonomy were determined in soil testing laboratories of CIAT (Center for Research in Tropical Agriculture) and chemistry laboratories of the University of Valle, using registered methodologies of IGAC[19] and USDA[20].

Adsorption studies of chlorpyrifos and diazinon

Determination ratio soil / solution. As the main interest is to quantify the amount of pesticide remaining in solution and adsorbed to soil, for this case where high concentration of organic carbon is present, moderate percentages of clay and high acidity, consider the analytical methodology to detect, remove and quantify the amounts of analyte in solution and in soil. Weber *et al.*[21] and Wauchupe *et al.*[7], propose to estimate the ratio soil / solution for an approximate $\mathbf{K}_d$ adsorption based on organic carbon content, pH and clay in the soil, in general for organic pesticides and in different soils; so K_d adsorption = 0.29 (% CO) + 0.17 (% clays)-0.13 pH, when $\mathbf{K}_d$ determined, ratio soil / solution appropriate for the adsorption percentage that is deemed for quantification technique is selected[22]. To assess K_d soils of three sampling points covering the maximum and minimum measured of CO and Clay of the study area were selected.

Determination of equilibrium time. The time in which the pesticide is applied to the soil reaches equilibrium between the different phases, that is, the time at which the concentration of the pesticide adsorbed to soil or dissolved in the solution remains constant was determined. Necessary step to validate the subsequent adsorption isotherm studies in which is required a period of continuous stirring of set Soil-pesticide, which must be greater than time needed to reach the equilibrium.

For this purpose, 1.0 g of each dry sieved soil (2 mm) was placed in each of 10 test tubes, was added 4.0 mL of pesticides chlorpyrifos and diazinon

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40 ppm dissolved in 0.01 M $CaCl_2$, to each tube tightly capped and subjected to rotating mechanical stirring constant moderate for 20 hours at 53 rpm, a tube was removed after each hour of stirring. Proceeded centrifuged at 10,000 rpm for 10 min, the supernatant is filtered and quantized to know the concentration of pesticides in the supernatant. The result obtained by analyzing the supernatant is the pesticide in the soil solution, and the difference between the initial concentration and the concentration in the supernatant, the concentration of adsorbed pesticide is determined.

Adsorption isotherms. Adsorption of pesticides in soils was performed by weighing 5 times and duplicate 1.0 g of each soil type, adding to each pair of tubes 4.0 mL of pesticides prepared in 0.01 M $CaCl_2$ concentrations 10, 20, 30, 40 and 50 ppm, so that each pair of tubes corresponds to initial concentration (i) of different pesticides, the solutions were placed in rotating mechanical stirring continuously for about 12 hours, sufficient for the pesticide reaches equilibrium. After this time the tubes were centrifuged at 10,000 rpm for 10 minutes, the supernatant was passed through 0.22 µm filter and finally its equilibrium concentration (Ce) is determined by gas chromatography. The difference between Ci and Ce is assumed due to the process of adsorption to soil (Cs).

Modelling of the adsorption isotherms. For the quantitative description of the adsorption processes, isotherms obtained experimentally were fitted to the logarithmic Freundlich equation. Similarly in all cases the distribution coefficient, $\mathbf{K}_d$ and normalized distribution coefficients to organic carbon content in the soil of study was calculated, **Koc** was calculated by dividing the adsorption coefficients $\mathbf{K}_d$ between the organic carbon content of each soil sample.

RESULTS AND DISCUSSIONS

Ratio soil/solution. Table 1. shows the characteristics of the soils studied and is recorded the results of the medium in organic carbon content, clay, pH profile and adsorption K_d adsorption estimated for adsorption between 50% and 80% of the pesticides to the soil, where it was determined that a 1/4 ratio (soil / solution), that is 1g soil / 4 mL of solution is appropriate for the the adsorption technique these pesticides in andic soils.

Equilibrium time, adsorption isotherms, adsorption coefficient. The equilibrium time for pesticide study in the percentages ranks of organic carbon was reached at 12 hours after initiation the experiment defining this as the minimum time to reach equilibrium.

Figure 1. presents the plots of the adsorption isotherms for chlorpyrifos and diazinon in each soil. A R^2 higher than 0.94 for diazinon pesticide in all cases were observed, while the R^2 for the pesticide chlorpyrifos ranging from 0.79 to 0.91. Given the shape and curvature of the isotherms

Table 1. Estimated kd adsorption and its relation soil / solution for adsorption of organophosphorus pesticides of 50%-80%

Soil	Porcentaje OC	Porcentaje Clay	pH	K_d*.100 Adsorption estimated	Ratio Soil/Solution	
					50%	80%
1	8,4	20,2	4,66	519	1/4	1/2
2	14,1	22,6	4,66	719	1/6	1/4
3	19,5	15,4	4,93	757	*1/6*	*1/4*

* Equation proposal to organophosphorus pesticides: Kd = 0,28 (%CO)+0.17 (%Clay)-0.13 pH and for soil adsorption of 50-80 %. Weber *et al*.[21], EPA[22].

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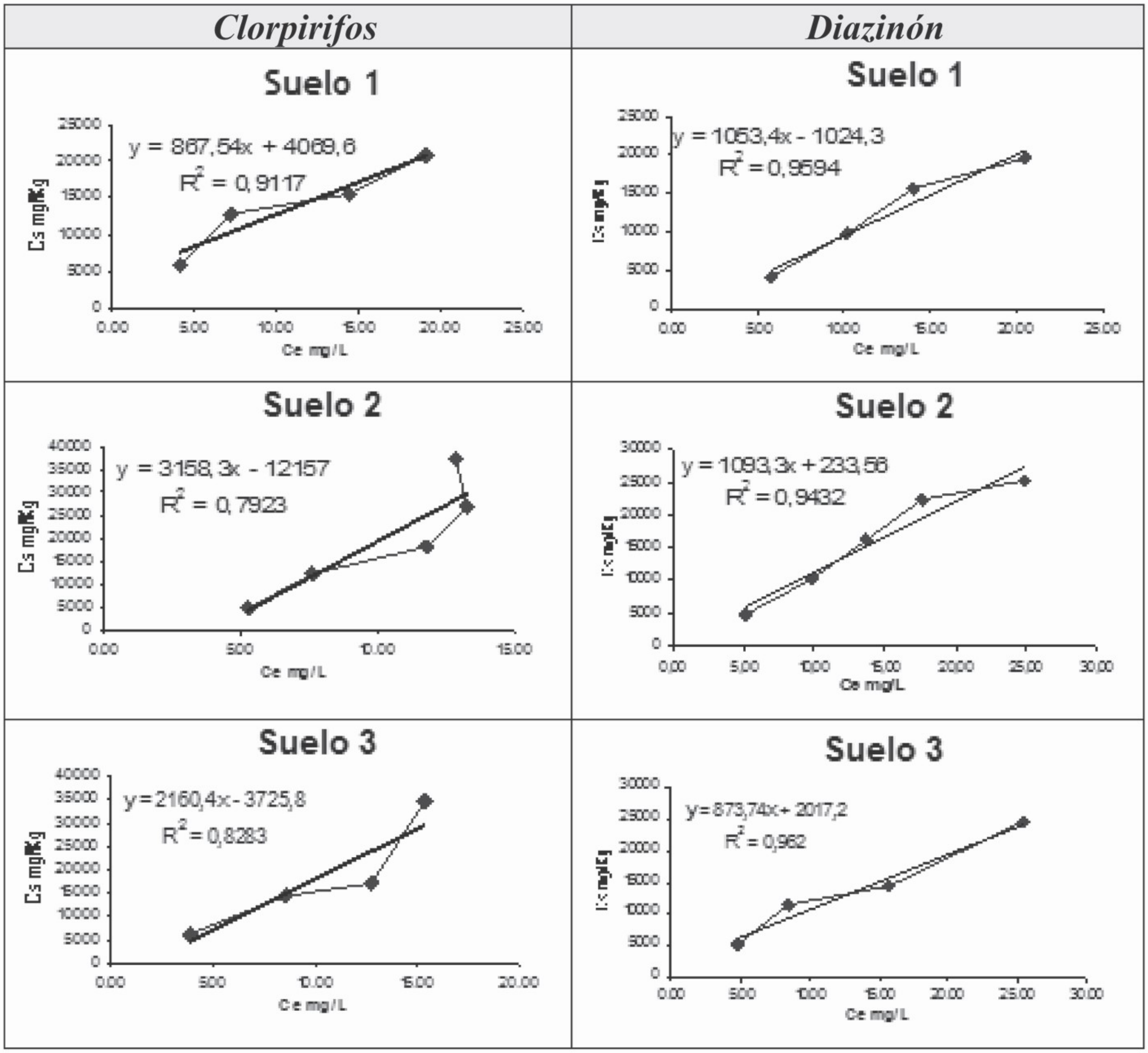

Figure 1. Adsorption isotherms of chlorpyrifos and diazinon

are classified as type C isotherms, characterized by a constant contribution of the affinity between pesticides and soil.

Although a slight tendency to type S isotherm is observed for the case of the pesticide chlorpyrifos, indicating that the adsorption between the pesticide, water and previously adsorbed molecules is relevant in this process.

Linearization of the isotherms by the Freundlich equation, adsorption constants, K_f were obtained and of they the adsorption constant K_{oc} according to the content of organic matter in soil.

In general the adsorption isotherms showed good linearity, diazinon adsorption perfectly adjusted to this model (R^2 of 0.92 to 0.97), while the pesticid chlorpyrifos provided R^2 between 0.90 to 0.92 (fig. 2), This is partly explained by the chemical structure of each of these pesticides and insertion of functional groups present in the soil organic matter.

Long Yu *et al.*[23], conclude that the behavior of chlorpyrifos in the adsorption-desorption processes are controlled by the content of SOM and its octanol-water partition coefficient. These compounds may form hydrogen bonds with soil humic substances and clay minerals by the free electrons of the atoms of sulfur, oxygen and nitrogen, latter atoms favors a high coefficient (close to 1) in the intensity of diazinon adsorption, gives larger size and a high electron affinity that does not allow to determine a tendency to about the adsorption intensity coefficient. This also indicates that the chlorpyrifos pesticide will have less intensity to penetrate the reactive sites of the organic matter, while for diazinon be facilitated.

Finally K_{oc} determined for chlorpyrifos and diazinon in andic soils were recorded between 8444 - 9943 and 5800 - 6300 respectively, literature values of 6070 to 1000 for chlorpyrifos and diazinon soil with organic matter not greater than 2% are reported, This makes us think that our experimental values agree with the values reported and given the specific characteristics of these soils.

The high absorption coefficient with both pesticides in andic soils is highlighted and high values of K_{oc} registered representing a high K_d and therefore such a high concentration of pesticides adsorbed to the soil as reported in Gebremariam *et al.*[24], in soils with high organic matter content. This can explain the composition given by extracts of organic matter in different state of humification on profile at different depths, high level of transformation of organic matter and environmental equilibrium conditions, physical and chemical of the area, which makes it work as a retainer, regulator and debugger all types of organic and inorganic compounds arriving there by natural phenomena or human activities. Figure 2.

Table-2 shows the parameters of adsorption, K_f and nf after isotherms adjusting to the Freundlich adsorption equation. K_f values in Chlorpyrifos higher than those reported by Tay Joo Hui *et al.*[24] in soils of Terengganu.

CONCLUSIONS

Adsorption of chlorpyrifos and diazinon pesticides in this type of Andic soil occurs in maximum 12 hours due to the high concentration of organic matter, neither pesticide was detected at more than 30 cm of soil depth, given the high concentration of organic matter adsorption occurs in surface soil layers: in the first 10 cm adsorbs 80% of applied chlorpyrifos and 60% of diazinon and small amounts reaching different depths Profile, are carried by the advective movement facilitated by high porosity and high hydraulic conductivity of the soil.

Therefore, these pesticides to be strongly adsorbed in the first centimeters of the soil, have a pattern of very low dissipation by leaching and a high risk of movement to different parts of the applied by effect of winds and surface runoff, which, together with persistent ($t_{1/2}$ = 85-122 for chlorpyrifos and $t_{1/2}$ = 42-53 days to diazinon) and tropical environmental conditions is facilitated. Is reiterated that climatic factors markedly affect the processes of adsorption, leaching, mobility and transport of these compounds and for the specific case of the pesticides chlorpyrifos and diazinon approximately 10% and 40% of the amount added to the soil with

Table 2. Adsorption coefficient (kf and nf) of chlorpyrifos and diazinon obtained from the freundlich equation and the value of koc (l / kg).

	Clorpirifos				***Diazinón***			
Soil	K_f	n_f	R^2	K_{oc}	K_f	n_f	R^2	K_{oc}
1	2385	1,35	0,91	8499	501	0,80	0,96	5897
2	227	0,53	0,92	9632	800	0,89	0,97	6301
3	1365	0,90	0,92	9451	1475	1,1	0,94	5896

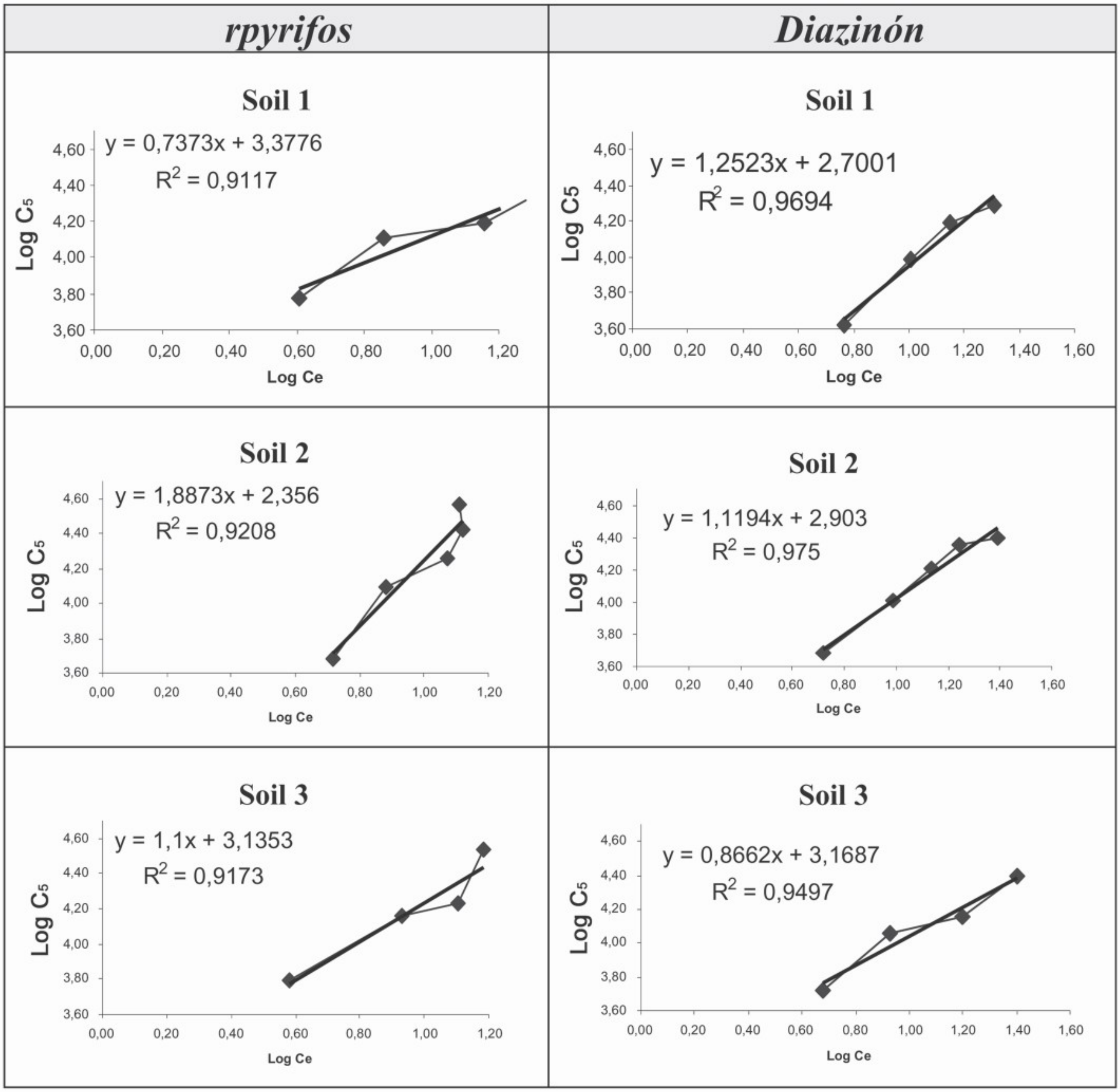

Figure 2. Linearized adsorption isotherms (Freundlich equation) for chlorpyrifos and diazinon in soils.

the andic characteristics reported remains without dissipating until after 130 days after applying the product.

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