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Sorption and Desorption of Cyhalofop-Butyl on Mesopotamic Agricultural Soils

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The ability of herbicides to be adsorbed by the soil and their tendency to be desorbed are some of the most important factors affecting soil and water contamination. Therefore, a sorption and desorption study were conducted to evaluate the adsorption-desorption of cyhalofop-butyl, in the sandy clay loam and at different depths using a batch equilibrium method. The adsorption of cyhalofop-butyl was found positively related with the clay and organic carbon content. The kinetic profiles occurred in three steps. With an initial rapid adsorption in the early hours followed by slow adsorption and then it was constant during the rest of the range studied. Adsorption data conformed well to the Freundlich isotherm, whit increasing of adsorption with increasing of organic matter of the soil of different depth. The desorption process showed an important hysteresis phenomenon. The adsorption isotherm suggested a relatively higher affinity of cyhalofop-butyl to the adsorption sites at low equilibrium concentrations. The low value of the soil organic carbon partition coefficient (K_{oc}) of cyhalofop-butyl in the sandy loam soil suggested its weaker adsorption in soil and thus increased its risk of mobility into water sources.

Introduction

Nowadays to satisfy the demand of production, the farmers need to implement methods of prevention and emergency against plagues that could affect his performance; one of these technologies is the use of pesticides

It is important to understand that on being applied any pesticide a process of interaction begins between this one and the ecosystem until it finishes its effect and disappears. This interaction includes the atmosphere, soil, water and plants. Some pesticides according to its structure and physicochemical features persist in the environment, promote their accumulation in water and soil mainly, reach after the chain tropic and finally arrive until the human organism.[1]

One of the components of great relevance in the agricultural production systems are the harmful species named undergrowth, in order to eliminate them and protect crops herbicides are used.

The herbicides are chemical products capable of altering the physiology of the plant causing the death or their abnormal development of the same one. The herbicides generate their lethal effects acting on a primary site of reaction and which can be followed by secondary, tertiary effects leading to the death of the plant.[2,3] The way of action of a herbicide consists of the sequence of events which occur since this one is absorbed by the plant up to the appearance of phytotoxicity.

Herbicides in their pure form have very little use for users (producers, farmers, agricultural technicians). Therefore, these substances need to be conditioned for use in agriculture, need to be formulated. The formulation is the way in which the pesticide is available for sale and use. The formulation is made in order to improve or enhance the properties of a herbicide as implementation, management, efficiency, storage and security. There are various types of formulations which are oil soluble, emulsifiable concentrate, wettable powder, liquid, granular dispersible, granular and lozenges.[4] The formulation is the physical mixture of one or more herbicides and inert ingredients, which provides effectiveness and controls weeds more economically. Each formulation has one or more chemical ingredients biologically active responsible for the action and effect of the herbicide and a carrier material which in commercial product is the vehicle. This materials, either liquid or solid in which are dissolved or distributed the active ingredient and additives, are substances which increase the action or favorably modify the action of the active ingredient (penetration, absorption, adhesion on foliage).[5,6]

For the formulation of a new product should take an important factor which may cause the product is efficient or not and is the physical and chemical nature of the active ingredient. This refers to that active ingredient of the formulation is soluble in various solvents such as water or other organic type and inert ingredient characteristics that not have biological activity.[5]

The cyhalofop-butyl (butyl (2R)-2-[4-(4-cyano-2-fluorophenoxy) phenoxy]propanoate, CyB) is a selective herbicide used for post-emergence control of grass weeds usually in rice crops. CyB is a member of the aryloxyphenoxy propionate class of herbicides. Like the majority of the compounds in this class,

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cyhalofop-butyl is readily absorbed by plant tissue, is phloem mobile and accumulates in the meristematic region of the plant. (Sterling et al, 1997). In addition, cyhalofop (acid) is an inhibitor of Acetyl-CoA carboxylase, which catalyzes the first committed step in fatty acid biosynthesis.[7]

The ability of herbicides to adsorb on soils and sediments and their tendency to desorbs are the most important factors affecting soil and water contamination. Adsorption depends on both molecule and soil physicochemical properties. In soil, the surfaces responsible for adsorption are colloidal particles and among those, are organic matter and clays. Organic matter, due to its chemical affinity with agrochemical molecules, has the greatest adsorption strength towards these species; high surface area and the interlayer charge of clays, such as expandable phyllosilicates, make these sorbents good for Organic molecules.

The strength of adsorption affects molecule mobility along the soil profile and thus, its bioactivity, persistence, biodegradation, leaching, and the volatilization process are affected too. The adsorption of an agrochemical onto the soil components can be considered as the first step towards its chemical degradation.

Organic molecule adsorption modeling by soils is frequently done using adsorption isotherms.

Soil metabolism studies indicate that cyhalofop-butyl is rapidly metabolized under both flooded and upland conditions. In soil mobility studies, cyhalofop-butyl is relatively immobile.

The prediction of the movement and the fate of herbicides in soils represent an important strategy in limiting their environmental impact. The physicochemical properties of herbicides affect their behavior in soil and regulate their interaction mechanisms with organic and inorganic soil phases. Among these, dissolved organic matter plays an important role, influences the mobility of herbicides by complex interactions that can facilitate or reduce the movement of chemicals along the soil profile.

The knowledge of soil phase characteristics and the mechanisms involved in herbicide transformation can help to understand the fate of herbicides in soil, therefore the objective of this work is to study the process of adsorption-desorption on the floor of a formulation of cyhalofop-butyl used in rice cultivation.

Results and Discussion

According to the determination of soil texture this was classified as sandy clay loam at all depths. The percentage of organic matter decreases in depth, while the percentage of clay remains constant at all depths (Table 1).

Sorption kinetics

The sorption is not almost instantaneous in the early hours of contact, and then increases progressively and quickly. This lack of balance can be explained by the existence of a first stage sorption CyB in accessible sites, followed by molecular diffusion to sites of this sorption less accessible as soil micropores or within of soil organic matter.

The kinetic profiles of all soils of different depths suggest that CyB absorbed through three stages: an initial rapid adsorption until the early hours followed by a slow adsorption and then remains constant.

The linearized form of equation 2 was used to fit the experimental data. Table 2 shows the fitted parameters. The experimental results at 25 °C and the fitted curves obtained are shown in Figure 1.

Table 1. Physico-chemical characteristics of the soils

Depth (cm)	pH	OC (%)	CIC meq/ 100 g	N (%)	Ca^{2+} meq/ 100 g	Mg^{2+} meq/ 100 g	K^{+} meq/ 100 g
0-10	6.53	2.78	21	0.49	8.5	3.0	0.30
10-20	6.62	1.67	22	0.36	10.5	7.0	0.25
20-30	6.60	1.11	25	0.21	11.5	4.5	0.23

Table 2. Constants of the CyB adsorption kinetics adjust to a two stage first order

Soil, depth (cm) Temperature(°C)	First step $k \times 10^{-5}\ s^{-1}$	Second step $k \times 10^{-5}\ s^{-1}$
0-10	7.42	1.34
10-20	7.35	1.16
20-30	7.06	0.98

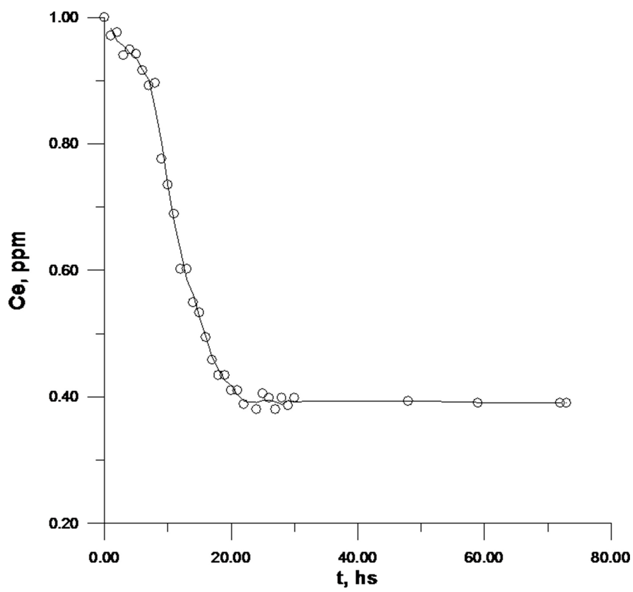

Figure 1. Adsorption kinetics of Cyhalofop-butyl to the depth 0–10 cm at 25 °C, showing the two step first order kinetic fitting.

Sorption isotherms

The absorption curves type in this work is L, the initial curvature shows that as more sites in the substrate are filled, it becomes increasingly difficult for solute to find an available vacant site. (see Figure 2) This result indicates that there are multiple interactions between the solute and the adsorbent; there is a strong molecular attraction between the solute molecules and little competition between the solute and solvent adsorption sites.

Sorption was studied in the arable soil at different depth and characterized through sorption isotherms (see Figure 2). Sorption isotherms were well described by the Freundlich equation with regression coefficients $R^2 > 0.99$; adsorption parameters (K_{fa} and $1/n_a$) are given in Table 3. (see Figure 3)

The empirical parameter, $1/n_a$, indicates the intensity of the adsorption process and traduces the affinity of the molecules for the soil sorbent. Also it shows that the adsorption is highly dependent on the initial concentration of the solution, with higher percentages of adsorption at lower concentrations. The value of $1/n_a$ (slope) <1 indicated a nonlinear relationship between the herbicide concentration and adsorption (Figure 2, Table 3).[8] The obtained values of K_{fa} indicate a decrease with depth and can be attributed to the decrease in organic matter. The not linearity of sorption isotherms in the range of concentrations studied justified the calculation of K_d and K_{oc} at a single concentration in order to compare the sorption capacities of the different soils depths. K_d values ranged from 1.08 to 2.07 L kg^{-1}.

The sorption coefficient (K_{oc}) was a measure of pesticide sorption, which, in association with soil organic matter, is commonly assumed to be a major mechanism of pesticide sorption in soils. Sorption coefficients (K_{oc}) were found between 45.53 and 121.06 in the different depth.

The K_f (Freundlich constant), K_d (distribution coefficient), 1/n (slope), and K_{oc} (organic carbon constant) values of cyhalofop-butyl in sandy clay loam are given in Table 3 for adsorption.

We observed a greater sorption of cyhalofop-butyl in the surface soil (0-10 cm) compared with the two horizons, and it was the lowest in the higher depth (20-30 cm). These results are in agreement with previous studies showing the predominant role of soil organic matter in herbicides adsorption.[9,10]

The soil organic matter quality present in the depths soil types could influence adsorption directly due to differences in chemical composition.[11] This supports the idea that the amount of C alone cannot explain the different sorptive properties of soils.[11,12] In our work the amount of organic matter is related to the increased adsorption of the herbicide.

In the different soil depths, other factors such as the nature of major cations bound to soil organic matter, the interactions between organic matter and mineral constituents or soil pH can influence herbicide sorption.[13,14,15] In the depth of 20–30 cm the adsorption of CyB was influenced by the clay content and cation exchange capacity of soil.[16]

We found higher K_{oc} values in the 20–30 cm depth, where the amount of organic carbon was the lowest. As already observed in temperate soils, the participation of mineral fractions, mainly clay minerals, in pesticide sorption was

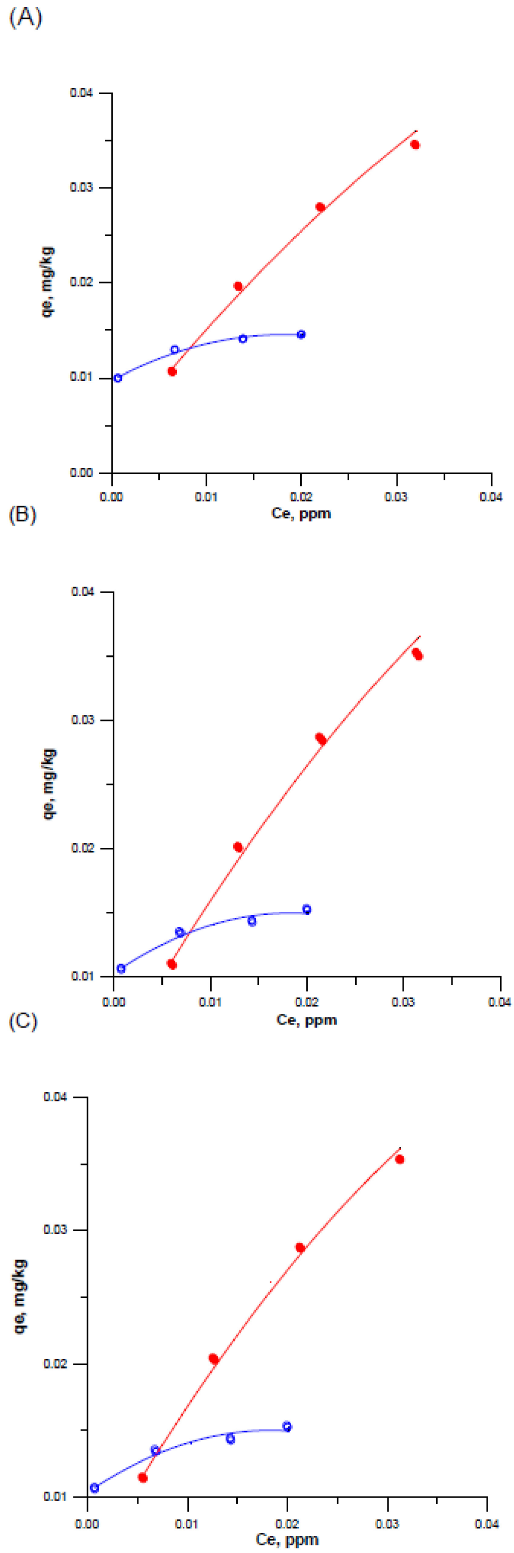

Figure 2. Sorption (plain red symbols) and desorption (empty bleu symbols) isotherms of Cyhalofop-butyl on the different depth soil. Plain and dottes lines correspond to the fitting using the Freundlich equation. (A) 0–10 cm, (B) 10–20 cm and (C) 20–30 cm respectively.

Table 3. Freundlich sorption coefficients (K_{fa}, n_a) and partition coefficients K_d and K_{oc} calculated for a solution concentration at equilibrium of 0.05 ppm. Values are means ± standard errors

Soil Horizon cm	K_{fa} L kg^{-1}	$1/n_a$	R^2	K_d L kg^{-1}	K_{OC} L kg^{-1}	Sorbet %
0-10	0.46 ± 0.005	0.74 ± 0.010	0.994	1.26 ± 0.01	45.53 ± 0.25	57.37 ± 4.5
10-20	0.42 ± 0.002	0.71 ± 0.008	0.994	1.33 ± 0.02	79.45 ± 1.1	58.80 ± 5.7
20-30	0.36 ± 0.014	0.66 ± 0.008	0.997	1.34 ± 0.02	121.06 ± 0.65	59.70 ± 5.5

suspected to increase when the soil organic matter content decreases.[12] The ratio of clay content to the organic carbon content (K) is a useful parameter to predict adsorption of herbicides in soil when decrease the organic matter.[17] The ratio K was found to be 8.74, 14.55 and 21.89 for the three horizons respectively.

The affinity of cyhalofop-butyl towards the clay content of the soils was also evaluated by calculating K_c using the formula:

$$K_C = (K_{fa}/c)\ 100 \qquad (1)$$

Where K_{fa} was the Freundlich constant and C was the percent of clay content in soil. The affinity of cyhalofop-butyl towards clay content (K_c) was found to be 1.89, 1.73 and 1.48 for the three horizons respectively. The sandy clay loam soil adsorbed a minor amount of cyhalofop-butyl per unit organic carbon; therefore, a less K_{oc} was found in sandy clay loam soil.

Desorption isotherms

Desorption isotherms presented hysteresis (see Figure 2) and fitted well to the Freundlich equation with regression coefficients greater than 0.99 (see Table 4). Hysteresis was constant at all depth (see Table 3). For all depth the hysteresis observed, suggesting that sorption irreversibility was the same and the amounts of desorbed cyhalofop-butyl after three desorptions, expressed as a percentage of initial sorbed amount, was the 63%.

Table 4. Freundlich desorption coefficients (K_{fd}, $1/n_d$), hysteresis index, H, calculated as the ratio nd/na and proportion of desorbed pesticide (% of initially sorbed). Values are means ± standard errors

Depth cm	K_{fd} (L kg$^{-1)}$	$1/n_d$	R^2	H	Desorbed proportion %
0-10	0.023 ± 0.006	0.11 ± 0.006	0.999	6.73 ± 0.01	62.91 ± 2.6
10-20	0.024 ± 0.006	0.12 ± 0.007	0.991	5.92 ± 0.01	62.90 ± 3.5
20-30	0.022 ± 0.004	0.11 ± 0.003	0.992	6.00 ± 0.00	63.09 ± 2.3

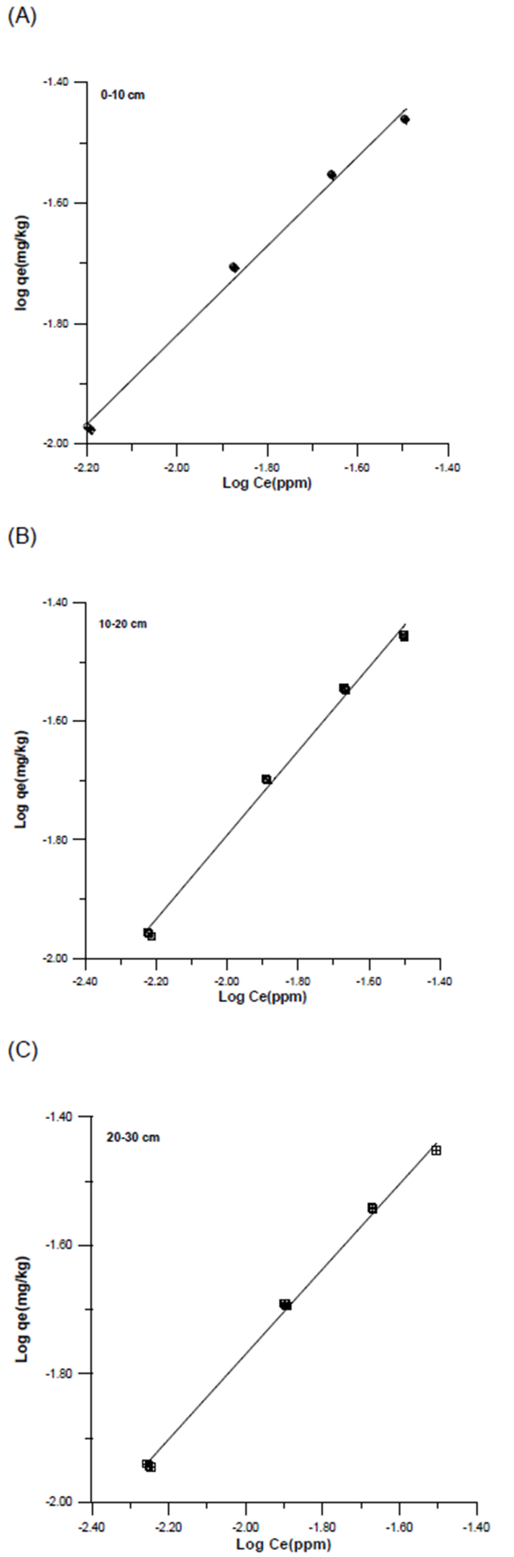

Figure 3. Freundlich adsorption isotherm for cyhalofop-butyl in sandy clay loam at different depths. (A) 0–10 cm, (B) 10–20 cm and (C) 20–30 cm respectively.

Conclusions

The adsorption of cyhalofop-butyl was found to be positively correlated with the soil clay and organic carbon content. The adsorption isotherm demonstrated a relatively higher affinity of the cyhalofop-butyl for the adsorption sites at low equilibrium concentrations in the soil. Hence, at normal equilibrium, it cannot be easily desorbed. It can be concluded that cyhalofop-butyl has low values of soil organic carbon partition coefficient (Koc) in the sandy loam soil, suggesting its weaker adsorption in soil and thus increased mobility into water sources. Hence, it should be used judiciously to prevent groundwater contamination especially near the aquatic sources.

Supporting Information

Experimental section.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Clay · Herbicide · Hysteresis · Soil · Sorption

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