



Adsorption of carbofuran on lateritic soils

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Abstract

Adsorption of carbofuran on the four selected lateritic soils is studied using batch experiments. Accordingly, the key influencing factors of carbofuran adsorption are determined. The adsorption isotherms on the lateritic soils correspond well with the Freundlich isotherm. The adsorbed amounts of carbofuran in toluene-and-bromoform treated soils (i.e. organic matter has been partly removed) follow nearly the same pattern as those in the original soils, and the adsorbed amount increases with the increase in soil pH, organic matter and clay contents. Also, the results show that the liming action and clay play important roles in carbofuran adsorption. The saturated adsorption maxima of carbofuran for the original soils are ca. 50% of the spiked amount. The distribution coefficient (K_d) increase with the increase in soil organic content and the solution/soil ratio. However, the low K_d obtained implies that carbofuran has a low affinity for the lateritic soil (i.e. more mobile). © 1998 Elsevier Science B.V.

Keywords: Carbofuran; Adsorption; Lateritic soil; Distribution coefficient

1. Introduction

Pesticides are commonly used to protect the grass from pest attack in golf courses. However, improper applications of pesticides create soil and groundwater pollution problems, resulting in not only the impact on the ecosystem but a risk to human health. The movement of pesticides and the adsorbability of soils are the two influencing factors that can be used to predict the contaminating level of the environment.

Most golf courses in Taiwan are built on the hill where the lateritic soils are classified. The lateritic soil that gradually formed due to a violent chemical weathering is rich in ferric and aluminum oxides with a red–brown color. Unfortunately, most of silicates and salts of calcium, magnesium, potassium and sodium are steadily swept from lateritic soil by a continuous weathering action. Consequently, the soil becomes acidic (i.e. pH 4.0–5.0) and reduces its cation exchange capacity (CEC) and organic content.

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The main clay minerals contained in the soil are kaolinite. For properly applying pesticides on golf courses and minimizing possibilities of the adverse effect on the environment, it is of great interest to study the behavior of pesticides in soil, which is governed by either physicochemical or biological action, especially, adsorption.

The mechanisms governing the fate of pesticides in soil are very complicated. Even so, the researchers need to account for the distribution of pesticide with depth of soil (i.e. dependant on pesticide movement and degradation rate) and the distribution coefficient (K_d) of pesticide between the aqueous phase and soil phase (i.e. pesticide adsorption). The two distributions are generally influenced by three factors: (1) pesticide properties, including its physical characteristics and susceptibility to chemical and microbial degradation; (2) soil properties, including its organic and clay contents, pH, depth, moisture, texture, and structure; (3) weather conditions, including the amount, frequency, and intensity of rainfall and temperature [1–4].

According to on-the-spot investigation, the pesticides commonly used in golf courses include carbofuran, prothos, chlorpyrifos, phorate, etc. Thus, carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate), commonly applied directly to soil or pasture that serves as insecticide–nematicide, is selected for this study. The half-life of carbofuran was reported more than 1 month [5].

Several researchers found that carbofuran is susceptible to leaching. For instances, McCall et al. [6] classified carbofuran as ‘highly mobile’. Lee et al. [7] assessed the behavior of eight major pesticides applied to the soils in Taiwan using mechanistic models, and found that carbofuran is most mobile. In addition, Osgerby [8] calculated the distribution (or partition) coefficient from the equation: $K_d = (\theta/\rho) - \theta$, where $K_d = (\mu\text{g of carbofuran/g of soil})/(\mu\text{g of carbofuran/ml of soil solution})$; ρ is the proportion of pesticide in soil solution; and θ is the fractional moisture content of soil (g of water/g of soil). Shelton and Parkin [9] found that a higher temperature would give a larger K_d value. Nicholls [2] offered that soil organic content well correlated with physical adsorbability of most pesticides. Harrod et al. [10] considered that the degree of hydration of organic matter can also influence adsorption of pesticides. The equilibrium sorption coefficients measured for carbofuran applied to two types of soils are 0.29–0.35 $\text{cm}^3 \text{g}^{-1}$ [11].

The extent of adsorbability of pesticides is an influencing factor to the potential of groundwater pollution as the pesticides are applied to the soil. The adsorption model commonly used involves the measurement of the partitioning of the pesticide between soil and water phases. The ratio calculated is defined as the distribution coefficient (K_d). Many studies have concluded that the soil organic carbon content is the most influencing factor to the extent of adsorbability of pesticides. This observation led to the concept of a compound-specific constant known as organic carbon partition coefficient (K_{oc}). K_{oc} is defined as the K_d of a particular soil/pesticide combination divided by the organic carbon content of the soil. The pesticide which has lower K_d and K_{oc} values is considered to be more mobile. Therefore, the constants which appeared in the adsorption models can be used to predict the transport of pesticide in the soil.

Specific objectives of this study are to evaluate the adsorption of carbofuran on the selected lateritic soils by conducting the batch experiments, and to determine which soil properties significantly influence sorption of carbofuran.

2. Materials and methods

The samples of lateritic soil without exposure to carbofuran were collected from four locations in the Taiwan Sugar Farm. The collected soil was then sliced off, finely diced, air-dried, and followed by sieved through a 2-mm screen before use. The four respective locations were differentiated by Site I, Site II, Site III, and Site IV, respectively. Soil texture of each soil was determined using the modified Bouvuccs hydrometer and Pipette methods [12]. Soil pH based on the soil–water suspension 1:1 (20 g soil:20 ml water) was determined using a glass membrane electrode [13]. Cation exchange capacity (CEC) was determined using sodium saturation method [14]. Organic carbon was determined using the modified Walkey–Black method (which titrates the solution with 0.5 N ferrous ammonium sulfate to substitute for ferrous sulfate, and the correction factor f is 1.45) [15]. The clay was occasionally analyzed by X-ray diffraction [16].

The carbofuran was analyzed by High Performance Liquid Chromatography (HPLC) according to the method given by Lauren [17]. This method can be used to directly determine the amount of carbofuran in the aqueous phase or methanol extraction phase. Filtration has to be performed before the determination of the amount of carbofuran remained in the aqueous phase. Also, methanol has to be used to extract the amount of carbofuran retained in the soil phase before hexane cleaning and HPLC analysis. Carbofuran was separated using a Spherex C8 column (5 μm particle size, 25 cm \times 4.0 mm ID) with the mobile phase of methanol and water (55: 45 v/v; flow rate 1 ml/min⁻¹), and it was monitored using a UV detector at the wavelength of 280 nm. The injection size was 100 μl . Under these analytical conditions, the detection limit of carbofuran was 60 $\mu\text{g/l}$, and the retention time was 7.5 min. Relative peak height for carbofuran decreased with the increase in methanol concentration of bulk solution. Thus, the stock solution of 2 mg/ml methanol was prepared, while the working standards in the ranges of 500 $\mu\text{g/ml}$ –0.1 $\mu\text{g/ml}$ were prepared in water.

2.1. Recovery of carbofuran

Each 10 g of soils collected from four different locations was first weighed and added into a 50-ml flask. Each sample soil was spiked at 10, 5, 1, and 0 $\mu\text{g/g}$ with 5 ml of appropriate concentrations of working standards. Duplicate samples were used for each soil. After standing overnight at 12°C, 20 ml methanol was added into soil sample which was immediately placed on a reciprocating shaker for 1 h. After settling (2 h), a 4 ml aliquot of extract was removed and mixed with 1 ml water and 2 ml *n*-hexane. Shake and let settle overnight. Another aliquot was removed and filtered using 0.2 μm filter paper. The filtrates were then analyzed for the residual carbofuran. Thus, the recovery of carbofuran can be calculated from the proportion of the residual and the applied. The experiments were repeatedly conducted for five times to ensure the validity of the results. Also, during the experiment, blanks were also prepared without adding the soil to see if carbofuran was adsorbed on the walls of flasks.

2.2. Adsorption vs. pH experiments (original soil)

Batch adsorption experiments were conducted to determine the amounts of carbofuran adsorbed on the original soil at different pH. The experimental procedures are

described as follows: into 45-ml polypropylene centrifuge tubes, 4 g of soil was added. The pH was then adjusted to between 4 and 10 using 10 ml various concentrations of $\text{Ca}(\text{OH})_2$ solution. Each sample was spiked at $20 \mu\text{g/g}$ with 10 ml of appropriate concentration working standard. According to preliminary experiments, the samples were equilibrated for 18 h at room temperature on a reciprocating shaker. Following equilibration, the samples were centrifuged (12000 rpm) for 10 min. (Sorvall RC-5B refrigerated superspeed centrifuge, SS-34 rotor). The supernatant solutions were then filtered using $0.2 \mu\text{m}$ filter papers. Thereafter, the filtrates were analyzed for the residual carbofuran. Thus, the amount of carbofuran sorbed on the soil can be calculated by the difference of carbofuran concentrations before and after equilibration.

2.3. Adsorption vs. pH experiments (toluene-and-bromoform treated soil)

The organic matter was partly removed from the soil samples using the specific gravity method, and the remaining part called treated soil was used. The specific gravity of a purely mineral soil varies between the narrow limits of 2.6 and 2.8. With the quantity of organic matter present, it may vary the specific gravity of any soil. As the specific gravity of organic matter usually ranges from 1.2 to 1.7, the more that is present, the lower will be the figure for any given soil [18]. So, they could be separated in the solution of specific gravity ca. 2.2–2.5. The solution of s.p. 2.3 was prepared using toluene (s.p. 0.86) and bromoform (s.p. 2.89). Soils were added into this solution (1:2), stirred completely, let stand for separation, and discarded the supernatant. The remaining part (i.e. treated soil) was filtered and air-dried in the fume hood. Batch adsorption experiments were then conducted to compare the adsorbability of carbofuran on original soils with that on treated soils at different pH. The experimental procedures used are similar to those described in Section 2.2.

2.4. Batch isotherm studies

The adsorption isotherm of carbofuran for various soil samples were repeatedly determined three times using the batch method. For each determination, 2, 4 or 10 g of air-dried soil was mixed with 20 ml of various carbofuran concentrations ranging from 5–50 $\mu\text{g/g}$. The soil samples were placed in 45-ml P.P. centrifuged tubes for 18 h shaking at room temperature. The suspensions were then centrifuged (12000 rpm) for 10 min, and the obtained supernatant solutions were filtered. Thereafter, the filtrates were analyzed for the residual carbofuran.

The experimental data obtained from batch isotherm studies were expected to fit the Freundlich isotherm that has the form: $\log x/m = \log K + n \log C_e$; where x/m represents the amount of carbofuran adsorbed on the soil (mg/g); C_e represents the equilibrium concentration of carbofuran in solution ($\mu\text{g/ml}$); and the constants K (intercept) and n (slope) obtained from linear regression are indicative of the adsorbability of carbofuran. The distribution coefficients (K_d) of the four soils were also calculated using the following adsorption model:

$$K_d = \frac{\sum \left(\frac{x}{m} \cdot C_e \right)}{\sum (C_e)^2}.$$

Table 1
Properties of soils used in this study

Measurement	Location of soil							
	Site I		Site II		Site III		Site IV	
	Original	Treated	Original	Treated	Original	Treated	Original	Treated
pH (1:1) ^a	5.0	5.1	4.3	4.2	4.5	4.5	4.7	4.8
OC (%) ^b	0.447	0.292	0.748	0.486	1.119	0.668	1.699	1.078
CEC (meq/100 g) ^c	8.70	2.25	11.65	3.52	18.35	5.26	17.52	5.72
Soil texture	Sandy loam		Clay loam		Clay		Silty clay loam	
Sand (%)	54		28		6		18	
Silt (%)	30		44		36		48	
Clay (%)	16		28		58		34	
<i>Main clay mineral^d</i>								
Kaolinite (%)	62.97		60.23		15.11		52.29	
Illite (%)	30.58		31.57		57.54		20.73	
Chlorite (%)	6.45		8.20		27.35		26.68	

^a1:1 = 20 g air-dried soil: 20 ml water.

^bOC: organic carbon.

^cCEC: cation exchange capacity.

^dThe total amount of the three main clay minerals was 100%.

In addition, the organic carbon partition coefficients (K_{oc}) were calculated using the equation: $K_{oc} = K_d/f_{oc}$; where f_{oc} represents the fraction of organic carbon in the soil and was measured, as shown in Table 1.

3. Results and discussion

Table 1 shows the physicochemical properties of the original and treated soils. The treated soils have been removed 35–45% of organic matter in the original soil. The removal organic matter belongs to aromatic part (fulvic acid), which makes more contribution to CEC. So, the CEC of the treated soils are more lower. The pH values of

Table 2
Recoveries of carbofuran from soils used in this study (%)

Samples	Recoveries (%)			Overall average (%)
	Carbofuran added ($\mu\text{g/g}$)			
	1	5	10	
Control	106.38 ± 9.38	102.25 ± 4.20	100.52 ± 6.37	103.18 ± 7.43
Site I	106.15 ± 7.63	99.85 ± 4.62	101.15 ± 4.10	102.33 ± 6.10
Site II	110.32 ± 4.09	103.10 ± 5.66	100.22 ± 1.74	103.97 ± 5.77
Site III	100.96 ± 1.36	105.57 ± 5.92	101.63 ± 3.10	102.70 ± 7.79
Site IV	106.10 ± 8.07	105.19 ± 5.21	98.46 ± 2.65	102.69 ± 6.46

the four lateritic soils used were ranged from 4.2–5.0. Also, the acidic soils had low organic content and CEC, and different soil texture. The main clay minerals found were kaolinite, illite and chlorite.

3.1. Recovery of carbofuran

Table 2 shows the recovery of carbofuran from four soil samples that spiked at three different levels. The recoveries were consistently high and ranged from 98 to 110%. Some researchers also found similar results [17].

3.2. Adsorption vs. pH (original soil)

The amount of carbofuran adsorbed by the original soil (Fig. 1) was significantly influenced by the pH. Under low pH conditions, only 2–17% of the amount of carbofuran was adsorbed by soil. However, the adsorbed amount increased to 10–40% and 40–50% as the soil pH were raised to 6.5–7.5 (neutral) and 7.5–8.5 (alkaline), respectively. Thus, the key influencing factors for carbofuran adsorption appeared to be pH. However, the saturated adsorption maxima of carbofuran for the four lateritic soils were about the same (i.e. ca. 50% of the spiked amount).

3.3. Adsorption vs. pH (treated soil)

The amounts of carbofuran sorbed in the treated soils (i.e. organic matter has been removed partly), as shown in Fig. 2, follow nearly the same pattern as those in the original soils (i.e. containing organic matter). The amounts of carbofuran adsorbed in the

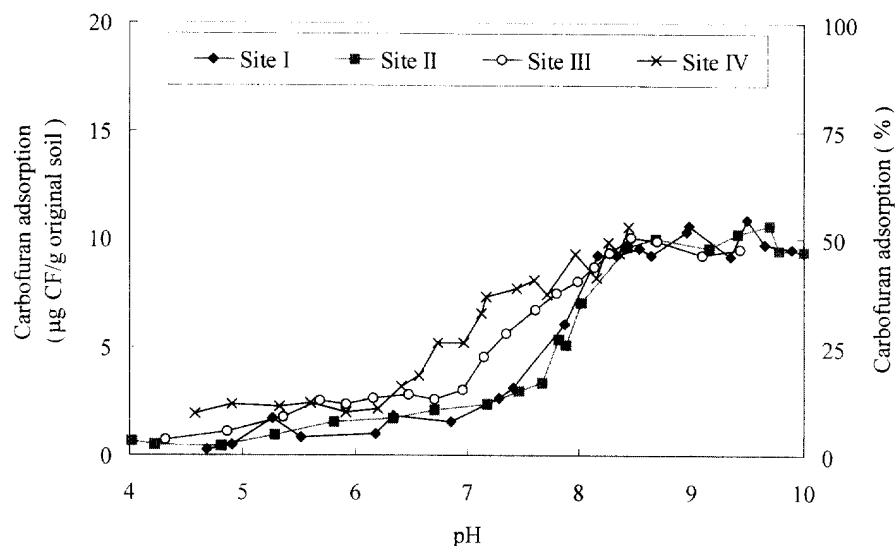


Fig. 1. Variations of carbofuran adsorption with various pH levels for original lateritic soils.

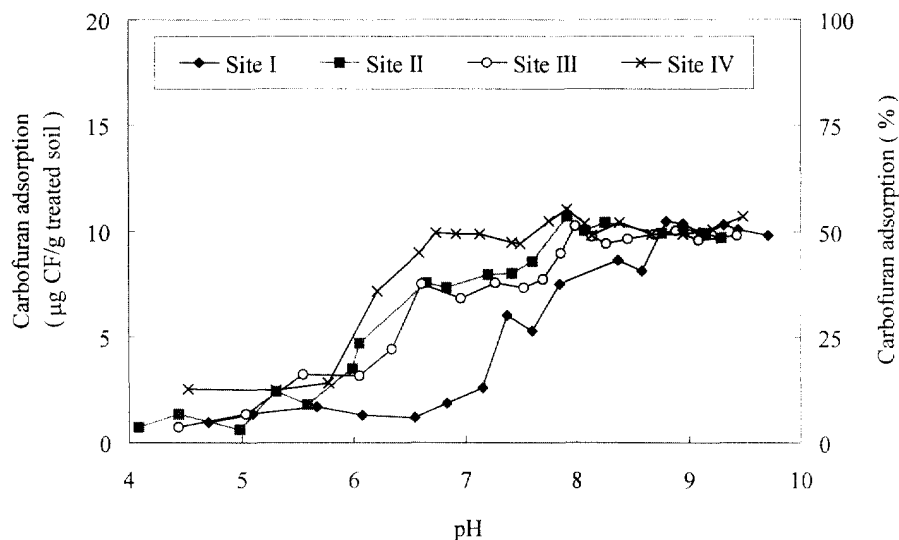


Fig. 2. Variations of carbofuran adsorption with various pH levels for treated lateritic soils.

original soil of Site I at various pH levels were no different from those in the treated soil. This may be because of low organic carbon contained in the Site I soil (i.e. only 0.447 and 0.292%). In contrast, the adsorption performance of the original and treated soils of Sites 2–4 at various pH levels were quite different, especially pH ranges of 6–8. At these pH ranges, the adsorbed amounts of treated soils were two- to four-fold the adsorbed amounts of original soils. Because the treated soil could attain the saturated adsorption under low pH conditions. Also, the organic matter contained in soils tended to lower the adsorbability of carbofuran. Hance [19] and Karickhoff [20] suggested that in soil, clay and organic matter associate in such a manner that little of clay mineral surface will be accessible to pesticide molecules. Thus, the contribution to adsorption of the clay fraction in soils would be much less than studies with the isolated mineral would indicate. The results in this study well agreed with Hance and Karickhoff on this point. On the other hand, Mortland [21] is of the opinion that organic compounds in soil, upon interaction with clay, may facilitate and stabilize adsorption of pesticides beyond that observed in purely inorganic clay systems. Relationships between organic matter and adsorption of carbofuran are discussed below in more detail.

3.4. Batch isotherm studies

The adsorption isotherms of carbofuran on the four lateritic soils well corresponded with Freundlich isotherm, and all r^2 values ranged from 0.87 to 0.99. The constants K and n of Freundlich isotherm and K_d values for the four lateritic soils under various solution/soil ratios are listed in Table 3. The calculated K_d values for the same soil increased with the increase in solution/soil ratio. The K_d values are also extremely dependent on the concentrations of carbofuran [22]. High K and low n values of Site IV

Table 3
Freundlich constants K , n and K_d , K_{oc} values for carbofuran under various solution/soil ratios

Location of soil	Ratio	K	n	r^2	K_d	K_{oc}
Site I	10/1	0.225	1.295	0.97	0.38	85.0
	5/1	0.130	1.2	0.996	0.19	42.5
	2/1	0.009	1.623	0.89	0.047	10.5
Site II	10/1	0.269	1.223	0.97	0.40	53.5
	5/1	0.206	1.019	0.97	0.22	29.4
	2/1	0.073	0.931	0.87	0.057	7.6
Site III	10/1	0.366	1.158	0.94	0.47	42.0
	5/1	0.223	1.029	0.98	0.24	21.4
	2/1	0.061	1.071	0.95	0.071	6.3
Site IV	10/1	0.875	1.026	0.96	0.97	57.1
	5/1	0.323	0.972	0.97	0.31	18.2
	2/1	0.246	0.888	0.98	0.177	10.4

soil (Table 3) indicated high adsorption of carbofuran on this type of soil, and the previous result as shown in Section 3.2 was further confirmed. Since K_{oc} is frequently used to characterize adsorption in pesticide transport models, the K_{oc} values of the four lateritic soils are also shown in Table 3. The K_{oc} values calculated for each soil at various solution/soil ratios were based on the K_d values and organic carbon data obtained in this study. The experimental sorption coefficients K_d and K_{oc} obtained in this study were well consistent to those obtained by other researchers [9,11,22,23].

Fig. 3 illustrates an alternative to estimate the K_{oc} values. In this figure, the linearized K_d was plotted as a function of the organic carbon fraction (f_{oc}). The K_{oc}

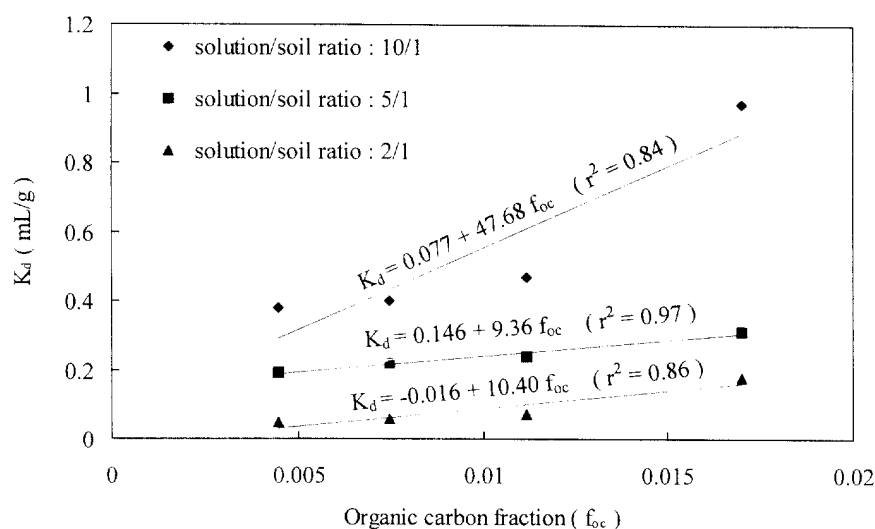


Fig. 3. Linear regression plots of K_d vs. organic carbon for carbofuran under various solution/soil ratios.

was then derived from the slope of the regression line. Meanwhile, the intercept derived represents the magnitude of K_d in the absence of organic carbon. It can be used to estimate the contribution of the mineral fraction to adsorption [22]. The slope-derived K_{oc} values vary with various solution/soil ratios. The high r^2 and low intercept for the solution/soil ratios 10/1 and 2/1 (Fig. 3) suggested that organic carbon played a primary role in carbofuran adsorption, and K_{oc} provided there is a satisfactory estimate of carbofuran adsorption. In contrast, the slope-derived K_{oc} value with a large intercept at the solution/soil ratio 5/1 is obviously different from the calculated K_{oc} (i.e. calculated by using K_d and f_{oc}). The results demonstrate that not only the mineral fraction cannot be ignored but that the fraction plays a major role in the sorption process.

According to our data (Figs. 1 and 2), the mineral fraction of soil was more effective to adsorb carbofuran in the test soils than the organic fraction at the solution/soil ratio 5:1. Especially, there existed a distinct discrepancy in soil pH ranged from 6 to 8. The interaction of calcium cation and clay or organic matter would affect carbofuran adsorption, particularly the cooperation of calcium cation and clay could adsorb more carbofuran molecules under neutral conditions.

4. Summary and conclusions

According to our data, the sorption potential of mineral surfaces in natural surface soils is blocked by organic matter. The extent to which clay minerals contribute to sorption depends on both the ratio of clay mineral to organic carbon fractions of the soil and on the nature of the organic sorbate. The type of soil clay becomes increasingly important when soil organic carbon contents are low. The adsorbed amount of carbofuran increases as the pH, and the saturated adsorption maxima of carbofuran for the four lateritic soils obtained were approximately 50% of the spiked amount. The key factors for carbofuran adsorption may vary with various solution/soil ratios, which might be attributed to differences in soil pH, clay mineralogy, organic matter chemistry, clay–organic complex, or a combination of these. The adsorption isotherm of carbofuran on the four lateritic soils well corresponds with Freundlich isotherm. Moreover, the K_d values increase as the soil organic content and the solution/soil ratio increase. The lower K_d values obtained implied that carbofuran had a lower affinity for the four lateritic soils, and thus, it is more mobile. In addition to select the adequate soils containing higher organic matter and clay, we could adjust the soil pH to 7.0–7.5 by liming to promote adsorption capacity of soil and reducing the amount of pesticide in the groundwater and the subsequent migration into waterways, etc.

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